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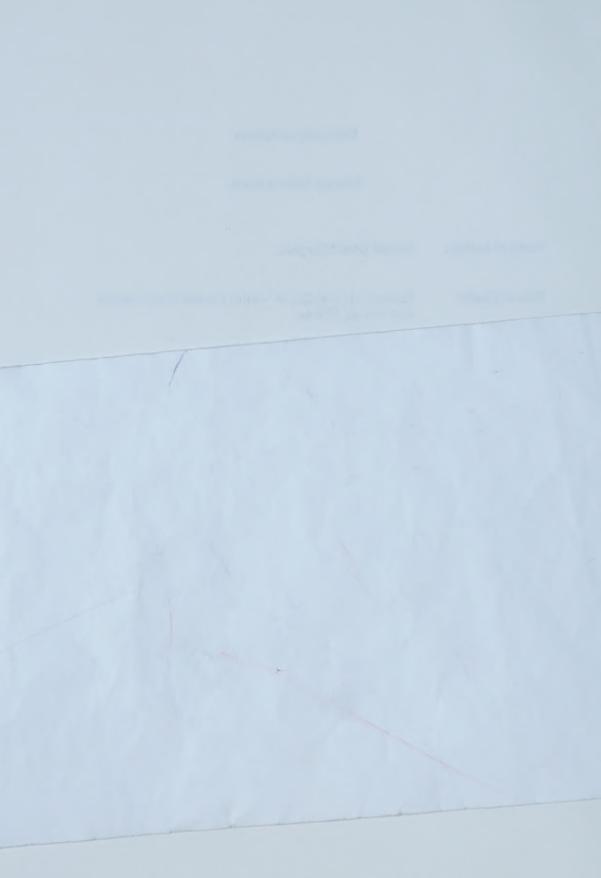
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University of Alberta

Personal Air Sampling of Volatile Organic Compounds in Fort McKay, Alberta

by

Russell Kenji Miyagawa (C)



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta

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University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Personal Air Sampling of Volatile Organic Compounds in Fort McKay, Alberta in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering.



Dedication

To my family, for you	our unconditional lov	e and support, and	your	everlasting	patience.
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Abstract

Fort McKay, Alberta is located near two large industrial facilities, with further development planned for the area. Sampling for selected volatile organic compounds (VOCs) was undertaken to gather baseline data, and examine factors influencing human exposure.

The study hypothesized that VOC levels: (1) are not significantly greater indoors than outdoors; (2) are not significantly greater in personal air than indoor air; and (3) are not significantly greater in winter than fall. Passive sampling of indoor, outdoor, and personal air was undertaken at 30 homes in Fort McKay.

Individual VOC concentrations ranged from undetectable to greater than 1000 $\mu g/m^3$. Wilcoxon signed rank tests indicated that VOC levels were much higher indoors than outdoors, and personal air levels were slightly higher than those found indoors. VOC levels were also higher in winter than fall. The results suggest that indoor sources and personal activities are dominant influences in determining exposure to VOCs.



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List of Symbols and Abbreviations

AB Alberta
ac air changes
A/C air conditioning

ATSDR Agency for Toxic Substances and Disease Registry

bpd barrels per day

BRI building related illness

BTEX benzene, toluene, ethylbenzene, xylene

C Centigrade CA California

CAT capillary adsorption tube

cm centimetre

CNS central nervous system

CS₂ carbon disulfide

d day

EPA Environmental Protection Agency

Eqn. equation

FGD flue gas desulfurization

GC/MS gas chromatography / mass spectrometry

GerES German Environmental Study

h hour

H₀ null hypothesis

H, alternative hypothesis

i.d. inside diameter ID identification

IDL instrumental detection limit

IPCS International Programme on Chemical Safety

km kilometre kPa kiloPascal

MDL method detection limit

m metre
mg milligram
min minute
mL millilitre
mm millimetre

NAS National Academy of Sciences

NC North Carolina
ND North Dakota
ng nanogram

NHEXAS National Human Exposure Assessment Survey

NJ New Jersey



o.d. outside diameter

OVM Organic Vapor Monitor
PEM personal exposure monitor

PERC tetrachloroethylene

PMCH perfluorinated methylcyclohexane

PVC polyvinyl chloride

QA/QC quality assurance / quality control

r_s Spearman rank-order correlation coefficient

RSD relative standard deviation SBS sick building syndrome s. d. standard deviation

sec second

SIM selected ion monitoring

t tonne

T+ Wlicoxon signed ranks test statistic

TCE trichloroethylene

TEAM Total Exposure Assessment Methodology

TWA time-weighted average

U. S. United States

VOC volatile organic compound

equal to
less than
greater than
percent
α alpha
μg microgram
μL microlitre



Chapter 1: Introduction

1.1 Background

It has been recognized that exposure to airborne pollutants poses a potential risk to human health, and that industrial activities are a significant source of pollutant emissions to the atmosphere. In order to assess the links between industrial pollution and human health, it is necessary to examine how industrial emissions contribute to human exposure to airborne pollutants. Anticipated increases in industrial emissions near Fort McKay, Alberta offer a unique opportunity to study the impact of these changes on community exposure to pollutants.

Fort McKay is a small community located relatively near to major industrial activities in the form of oil sands mining, bitumen extraction, and synthetic crude oil production at the Syncrude and Suncor facilities. These facilities emit a variety of pollutants including a number of volatile organic compounds (VOCs). The residents of Fort McKay have expressed concerns about the impacts of these emissions on air quality in their community, and the effects of exposure to these emissions on their health (Fort McKay Environment Services Ltd., 1996).

In light of the residents' concerns and planned increases in industrial activity in the area, there was both a need and an opportunity to study the impacts of industrial emissions on air quality and human exposure to airborne pollutants in Fort McKay. The measurements included in this thesis represent the first phase of a two-part study. In the second phase, a similar set of exposure measurements will be made subsequent to the increase in industrial activity and compared to the baseline measurements collected during the first phase. Given this comparison, the impacts of increased industrial emissions on air quality and human exposure will be assessed.



The main objectives of the first phase of the study were to:

- obtain baseline measurements of selected VOCs in personal, indoor, and outdoor air;
- examine the relationships between concentrations of selected VOCs in personal,
 indoor, and outdoor air;
- examine the factors affecting human exposure to VOCs; and
- improve the understanding of the sources and underlying causes of exposure to VOCs
 in Fort McKay.

1.2 Description of Study Area

1.2.1 Community Description

Fort McKay is located about 60 km north of Fort McMurray, which is around 450 km northeast of Edmonton (see Figure 1-1). The population of the community is around 330 people residing in 130 residences. Housing in the community consists mainly of single-family dwellings including a substantial number of mobile homes.

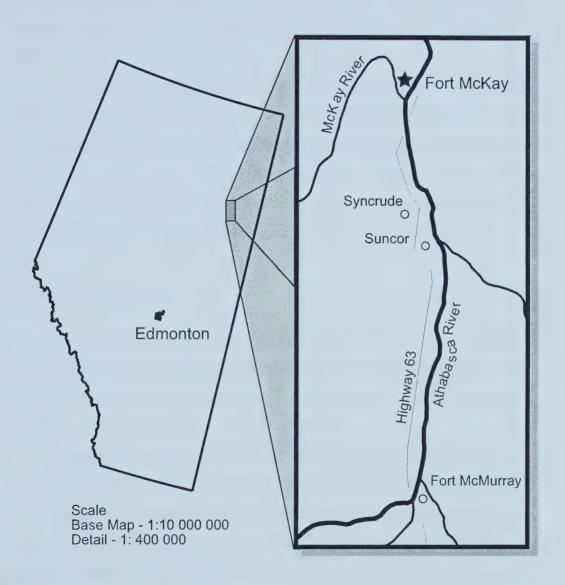
Fort McKay is located 16 km and 22 km from the Syncrude main stack and the Suncor powerhouse stack respectively (Golder Associates Ltd. et al., 1998). It should be noted that the edges of the Syncrude and Suncor properties are somewhat closer to the community. Figure 1-1 shows the relative position of the Syncrude and Suncor facilities to Fort McKay.

1.2.2 Industrial Activity

At present, the Syncrude and Suncor facilities are the primary industrial sources of VOC emissions in the Fort McKay region. Other industrial sources contribute significantly smaller amounts of emissions and are further from the community.

Oil production in the region of Fort McKay currently stands at around 300 000 barrels per day (bpd) primarily at the Syncrude and Suncor sites. By 2002, expansion at existing facilities will result in an increase in production to an estimated 400 000 bpd. It





Base Map Data © 2000. Government of Canada with permission from Natural Resources Canada

Figure 1-1 Map of Fort McKay region



is anticipated that continued expansion and new development in the area will further increase production rates to greater than 800 000 bpd by 2015 (Shell, 1997; Suncor, 1998).

Accompanying this increase in production will be an increase in VOC emissions. Suncor (1998) has estimated that its emissions of VOCs will increase from about 130 t/d to 240 t/d and that total VOC emissions in the region may increase from about 170 t/d to 380 t/d. Annual average total ambient VOC concentrations in Fort McKay are predicted to rise from 130 mg/m³ (based on emissions from existing and approved projects) to 226 mg/m³, assuming that all approved and planned projects become operational (Suncor 2000).

1.3 Research Hypotheses

The main hypothesis to be examined in the study is that increases in emissions from oil sands activities do not result in significant increases in levels of human exposure to VOCs. Although this hypothesis cannot be tested during this first phase of the study, it still forms a primary consideration into the study's design.

Although the main study hypothesis will not be tested until future measurements are taken, the study was designed to allow the testing of several secondary hypotheses:

Hypothesis 1: Concentrations of VOCs in indoor air are greater than outdoor concentrations. Review of previous studies indicates that indoor levels are typically higher than outdoor levels. This has been attributed in part to the presence of indoor sources of VOCs (De Bortoli et al., 1986; Lebret et al., 1986).

Hypothesis 2: Time-activity studies have indicated that most people in Canada spend a great majority of their time in indoor environments, most prominently inside their own homes (Leech et al., 1996). It follows that concentrations of air pollutants in the air that people breathe should be closely related to the concentrations of pollutants in the air inside of their homes. This leads to the hypothesis that concentrations of VOCs in



personal air are not significantly greater than, and are closely related to concentrations of VOCs in the air inside of personal residences. Studies have supported this hypothesis, but have also indicated that personal activities can have a significant effect on levels of VOCs in personal air (Wallace, 1987).

Hypothesis 3: Previous studies have indicated that VOC levels in outdoor, indoor, and personal air are greatest during the winter season (Seifert and Abraham, 1989; Hartwell et al., 1992; Cheng et al., 1997). For this study, we hypothesize that winter VOC concentrations are significantly greater than those found during the fall sampling season.

1.4 Methodology Overview

The baseline measurements obtained in this stage of the study will be compared to similar measurements taken after the expansion of oil sands activities. In order to ensure a statistically meaningful comparison, a probability sampling approach was adopted. This will allow comparison of the baseline results (i.e., the results of this study) to future measurements without having to revisit the exact same locations where samples were taken.

Prior to the beginning of the study, a letter was delivered to all homes in Fort McKay to make the residents aware of the study and its intent. A probability sample of homes was randomly drawn from the community to identify potential participants. Field workers visited the homes identified by the sampling process to explain the study and answer any questions that the residents might have. This process continued until 30 willing participants were identified.

Passive VOC sampling badges were deployed inside and outside of participants' homes, as well as in the breathing zone of one individual residing at each home. The personal sampler and one indoor sampler were retrieved after 24 hours of exposure. A second indoor sampler and the outdoor sampler were removed after 96 hours. The badges were sent to the Centre for Toxicology in Calgary, Alberta for analysis on a weekly basis.



During the fall sampling period, air exchange measurements were also made using a chemical tracer and passive sampler. These were deployed and removed at the same time as the VOC samplers.

In addition to the air sampling, participants completed a number of questionnaires regarding household characteristics and activities. During the first visit to the home, the participants supplied information on household characteristics such as the size and age of their homes, and types of heating systems present. At the time of the second visit when personal and indoor samplers were retrieved, questions were asked of activities inside of the home during the previous 24 hours. As well, the individual wearing the personal sampler was asked to complete a time-activity diary for the 24-hour period. During the third visit, when the remaining samplers were picked up, a questionnaire dealing with activities inside of the home during the previous 96 hours was completed.

The same homes were visited during the winter sampling period and similar sampling procedures were undertaken, with the exception of the air exchange measurements.



Chapter 2: Literature Review

2.1 Volatile Organic Compounds

The Oxford English Dictionary (OED) (1989) defines volatile as "characterized by a natural tendency to dispersion in fumes or vapor liable to, or susceptible of, evaporation and diffusion, at ordinary temperatures." The OED (1989) further defines that organic compounds "contain or are derived from hydrocarbon radicals." Volatile organic compounds (VOCs), therefore, are a class of hydrocarbon compounds that tend to partition into a vapor phase at room temperatures.

Typical properties of VOCs include low molecular weight, low boiling point, and high vapor pressure (Wang et al., 1996). Lewis (1989) proposed that compounds with vapor pressures greater than 10⁻² kPa at 25°C be classified as volatile. Many VOCs are highly reactive in the atmosphere and are implicated in the formation of ground-level ozone and photochemical smog (Hewitt, 1999).

VOCs are distributed throughout a variety of environmental media including the atmosphere, surface and ground water, soil, animals, and vegetation (Cohen, 1996). In terms of human exposure, inhalation is the dominant pathway for most VOCs. The US Environmental Protection Agency (EPA) Total Exposure Assessment Methodology (TEAM) study indicated that inhaled air accounted for greater than 99% of total exposure to the VOCs studied (Wallace, 1987a).

In 1988, the US EPA maintained database containing 300 VOCs identified in indoor and outdoor air (Shah and Singh, 1988). By 1998, the number had grown to over 1000 different compounds (Miller and Miller, 1998).

2.1.1 Health Effects

Exposure to airborne VOCs has been associated with discomfort or more serious health effects (Otson and Fellin, 1992). Outcomes identified as resulting from exposure to



individual compounds include cancer, behavioral and neurotoxic effects, hepatoxic effects, and sensory irritation (Berry, 1991). Knowledge of the effects of individual VOCs are often largely based on epidemiological studies of occupationally-exposed workers, where concentrations are much greater than those typically found in ambient or indoor air (Sterling, 1985). Carcinogenic and mutagenic effects in bacteria have also been demonstrated for some VOCs (Sterling, 1985). The effects of chronic exposure to low-level mixtures of VOCs are less well known and characterized.

Amongst the health outcomes associated with exposure to VOCs, cancer is of great concern due to its serious and potentially fatal nature. Based on the results of the TEAM studies, Wallace (1991) estimated upper-bound lifetime cancer risks associated with exposure to 12 VOCs. These estimates are summarized in Table 2-1. Due to the widespread exposure of the population to benzene, the associated cancer risk is of particular concern (Berry, 1991). Wallace (1989) estimated that exposure to benzene results in about 1000 excess leukemia cases annually in the United States. Berry (1991) reported that exposure to formaldehyde in the United States results in an estimated 300 excess cases of nasal cancer annually.

Other widespread health effects resulting from exposure to VOCs include the various symptoms which are often grouped together as "sick building syndrome" (SBS). Symptoms of SBS include (Mølhave et al., 1986):

- irritation of eye, nose, and throat;
- dry mucous membranes and skin;
- erythema;
- mental fatigue, headache;
- airway infections, cough;
- hoarseness of voice, wheezing;
- unspecific hypersensitivity reactions; and
- nausea, dizziness.

Mølhave et al. (1986) exposed 62 subjects to a mixture of 22 VOCs at three total concentrations: 0, 5, and 25 mg/m³. Significant effects of exposure were observed



Table 2-1 Upper-bound lifetime cancer risks for selected compounds (Wallace, 1991)

	Exposure	Potency	Risk
Compound	μg/m³	$(\mu g/m^3)^{-1} \times 10^{-6}$	x 10 ⁻⁶
benzene			
air	15	8	120
smokers	90	8	720
vinylidene chloride	6.5	50	320
chloroform			
air	3	23	70
showers (inhalation)	2	23	50
water	30 μg/L	2.3 μg/L	70
food & beverages	30 μg/L	2.3 μg/L	70
p-dichlorobenzene	22	4	90
1,2-dibromomethane	0.05	510	25
methylene chloride	6	4	24
carbon tetrachloride	1	15	15
tetrachloroethylene	15	0.6	9
trichloroethylene	7	1.3	9
styrene			
air	1	0.3	0.3
smokers	6	0.3	2
1,2-dichloroethane	0.5	7	4
1,1,1-trichloroethane	30	0.003	0.1

including degraded air quality, increased odor, decreased concentration, and mucous membrane irritation.

Kjægaard et al. (1991) repeated the experiment with 21 healthy subjects and 14 subjects suffering from SBS. While both groups reported worse air quality, worse odor, and more irritation of the mucous membranes; the SBS subjects tended to have a stronger response. A reduction in lung function due to exposure was also observed in the SBS subjects. Psychological tests indicated a decreased ability to learn related to exposure to a VOC mixture.

Testing of a group of 66 healthy young males with no history of chemical sensitivity showed that exposure to a mixture VOCs did not affect performance on 13



neurobehavioral tests, although increased fatigue and mental confusion were reported (Otto et al., 1992). Increases in eye and throat irritation, headache, and drowsiness were observed in the same group of subjects (Hudnell et al., 1992). Koren et al. (1992) observed a significant increase in inflammatory response in the nasal passages of 14 subjects exposed to a VOC mixture. Norbäck et al. (1995) reported a statistically significant relationship between indoor concentrations of VOCs and asthma-related symptoms in 88 Swedish subjects.

Sterling (1985) identified several considerations in assessing health effects from exposure to indoor levels of VOCs:

- exposure to VOC mixtures may result in additive or synergistic effects;
- the effects of chronic exposure to low levels of VOCs are not well-known;
- the exposed population varies in age, sex, susceptibility, and lifestyle;
- odors due to the presence of VOCs are both a source of complaints, and stressors which may increase susceptibility to other agents;
- exposure to VOCs may increase susceptibility to other agents; and
- sensitization and allergic reactions to various compounds may occur over time.

2.1.2 Outdoor Sources

VOCs in the atmosphere originate from a variety of natural and man-made sources. Major sources include combustion processes, fossil fuel production, organic solvents, industrial sources, and biogenic sources (Hewitt, 1999).

2.1.2.1 Natural Emissions

Emissions from plant foliage are a significant source of VOCs in the atmosphere (Guenther et al., 1993). Lamb et al. (1987) estimated that such biogenic emissions account for half of the total US emissions of VOCs. Muller (1992) suggested that emissions from plants account for two-thirds of total global VOC emissions. The major classes of foliar VOC emissions are isoprenes and monoterpenes, but numerous other VOCs, including alkanes, alkenes, alcohols, aldehydes, acetates, ketones, ethers, and



esters have also been identified (Guenther et al., 1993). Releases from forest fires and other biomass burning are also a major global source of VOCs (Singh and Zimmerman, 1992).

Oceans are another source of global VOC emissions, especially light hydrocarbons (Singh and Zimmerman, 1992). Major components of oceanic hydrocarbon emissions are ethylene and propylene, with ethane and propane forming much of the remainder.

2.1.2.2 Automotive Emissions

The US EPA TEAM study indicated that automobile use was strongly associated to personal exposure to benzene, m- and p-xylenes, and ethylbenzene (Wallace, 1987a). Driving or riding in automobiles, and exposure to vehicle exhausts have been identified as significant contributors to total exposure to benzene (Wallace, 1989). Seifert and Abraham (1982) found concentrations of BTEX compounds were much higher at a Berlin traffic intersection than those found inside residences or outdoors next to dwellings. It has been estimated that mobile sources account for 32% of US VOC emissions, and the contribution of vehicle emissions may be even higher in heavily urbanized areas (Cohen, 1996).

Studies of commuters' exposure to VOCs have found elevated levels of VOCs inside of automobiles as compared to ambient air. Löfgren et al. (1991) found that concentrations of eleven VOCs found in gasoline were 7 times higher inside cars than in the compartments of passenger trains. Chan et al. (1991) found that VOC concentrations while commuting (by car, subway, bicycle, and on-foot) were 3-5 times higher than concentrations inside homes and offices, with the highest levels associated with car commuting. Levels of exposure to VOCs while commuting by bus have been found to be lower than those while commuting by car or motorcycle (Chan et al., 1993; Jo and Choi, 1996). The latter study also indicated that exposures were greater when commuting in



urban areas as compared to suburban areas (Jo and Choi, 1996).

Automotive emissions can also impact VOC levels inside of homes. Gasoline vapors are virtually ubiquitous in houses with attached garages (Gammage and Matthews, 1988). The presence of gasoline vapors is due to both the storage of petroleum products and the operation of motor vehicles inside of the garage.

2.1.2.3 Industrial Emissions

While automobile emissions are likely the largest single source of anthropogenic VOC emissions in urban areas, total emissions from stationary industrial sources are often much greater, especially in areas without heavy traffic (Cohen, 1996). Studies have tended to show that ambient VOC concentrations are positively correlated with industrial emission rates (Cohen, 1996). The US EPA TEAM study of the early and mid-1980s found dramatically lower outdoor VOC concentrations in a community (Greensboro, NC) without major chemical manufacturing or petroleum refining activities and in a small rural town (Devils Lake, ND) than in more heavily urbanized and industrialized communities in New Jersey and California (Hartwell et al., 1987a). However, based on the New Jersey results, the study authors also concluded that residence near major point sources had little or no effect on personal exposures to VOCs (Wallace et al., 1986).

Fort McKay is a small community without the influence of heavy vehicle traffic, so industrial emissions are likely more significant sources of VOCs than vehicle emissions. Most of the vehicular activity in the region occurs south of the community between the existing Syncrude and Suncor sites and Fort McMurray. Industrial development north of Fort McKay will likely bring increased vehicular traffic adjacent to the community as well as increased industrial emissions.

The primary industrial sources of VOC emissions near Fort McKay are the Syncrude and Suncor facilities. The types of VOCs identified in these emissions include a wide range of straight-chain and branched alkanes, aromatics, and other compounds



(Golder Associates Ltd. et al., 1998). At these sites, emissions originate from a variety of sources such as fixed plant combustion, fixed plant fugitive emissions, vehicle emissions from the mining fleet, off-gassing from open mine faces, and off-gassing from tailings ponds (Suncor, 2000). Table 2-2 summarizes total VOC emissions from the Syncrude and Suncor facilities. From the table, it is evident that the tailings ponds are the largest emitters of VOCs to the atmosphere. It should be noted that in calculating their tailings ponds emissions, Suncor conservatively assumes that all VOCs entering the pond are released to the atmosphere although studies indicate that about 60% of VOCs are sequestered by fine particles in the tailings (Suncor, 2000).

2.1.3 Indoor Sources

Studies of indoor and outdoor concentrations of VOCs have typically pointed to the existence of indoor sources (Jarke et al., 1981; de Bortoli et al., 1986; Lebret et al., 1986). Personal activities, consumer products, and building materials can lead to both short-term and long-term emissions of VOCs (Gammage and Matthews, 1988). Otson (1996) identified potential sources of VOCs inside of Canadian residences. Table 2-3 summarizes possible indoor sources and the associated VOCs.

2.1.3.1 Tobacco Smoke

Tobacco smoke has been implicated as a major source of human exposure to benzene and other aromatics (Wallace et al., 1987a). Wallace (1989) estimated that about 50% of the total US population exposure to benzene could be attributed to tobacco smoke. Levels of benzene and styrene measured in the breath of cigarette smokers were found to be 5-10 times the levels found in the breath of nonsmokers, and levels inside the homes of smokers were slightly elevated (Wallace et al., 1989).

Exposure to sidestream smoke also results in increased levels of benzene and other aromatics in the breath of nonsmokers (Wallace et al., 1987a). Personal air



Table 2-2 Estimated VOC emissions from existing and approved oil sands projects (Suncor, 2000)

Suncor Base Plant Emissions		
Source	VOC Emissions (t/d)	
powerhouse stack	0.01	
FGD stack	0.15	
incinerators	0.21	
flaring	0.04	
secondary sources	0.08	
mine fleet	0.80	
fixed plant fugitive	23.5	
tailings ponds	200	
mine surface	8.10	
Suncor Total	233	

Syncrude Emissions		
Source VOC Emissio		
main stack	0.00	
8-3 diverter stack	0.00	
secondary sources	0.30	
fugitives	7:19	
mine fleet	1.11	
tailings ponds	43.7	
mine surface	8.64	
Aurora North	0.03	
Syncrude Total	60.9	

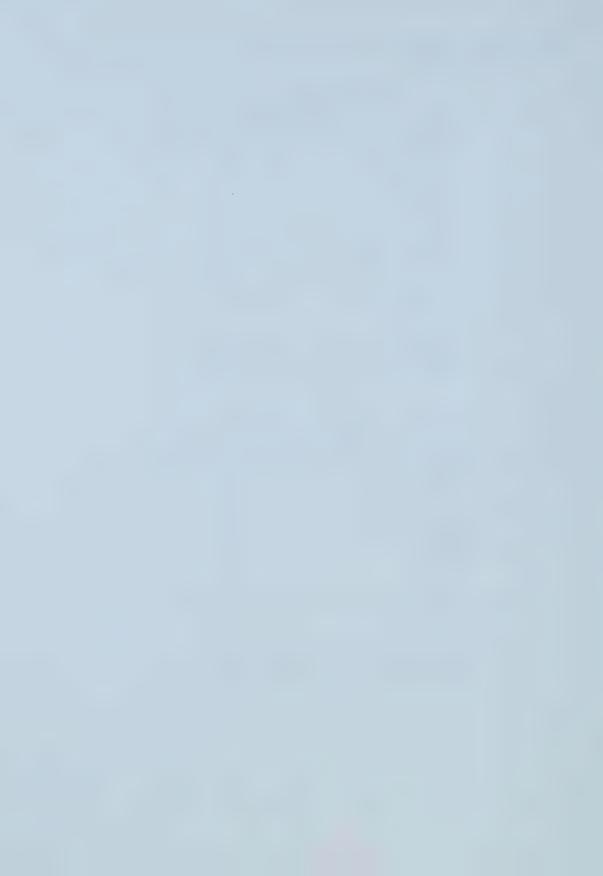


Table 2-3 Possible VOC sources and associated components (Otson, 1996)

Source	Components
Latex paints	benzene, 1,2,4- & 1,3,5-trimethylbenzenes, toluene
Alkyd paints	1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene
Carpets	1,2,4- & 1,3,5-trimethylbenzenes,benzene, toluene, styrene
Glued carpets	p-dichlorobenzene, n-decane
Wood burning	xylenes, 1,2,4- & 1,3,5-trimethylbenzenes, naphthalene, toluene, styrene
Foam board	dichloromethane, dichlorobenzenes
Paint removers	dichloromethane, toluene
Spray products	dichloromethane, xylenes
Adhesives / tape	trichloroethylene
Adhesives / tape	n-decane, toluene, styrene
Room deodorizers	p-dichlorobenzene, limonene, decane
Detergents	limonene, pinene
Waxes	pinene
Tobacco smoke	benzene, toluene, m- and p-xylenes, styrene, ethylbenzene
Gasoline / driving	benzene, toluene, xylenes, styrene, trimethylbenzene
Solvents	toluene, ethylbenzene
Dry cleaning	tetrachloroethylene
Tap water	chloroform

exposures to benzene and styrene were found to be 50% greater for nonsmokers living in homes with smokers than those living in nonsmoking homes (Wallace et al., 1989).

Lebret et al. (1986) found substantially higher concentrations of straight-chain and aromatic hydrocarbons in smokers' homes than in nonsmokers' homes.

2.1.3.2 Other Combustion Sources

Combustion processes have been identified as a potential source of VOCs indoors. VOCs are found in the exhaust gases of combustion appliances such as furnaces, ranges, space heaters, stoves, and fireplaces which may burn a variety of fuels (Otson and Fellin, 1992). Contamination of indoor air may occur directly through leaks in the vent



system, or indirectly through the infiltration of exhaust gases from the outdoors. Otson and Fellin (1992) reviewed the literature pertaining to combustion appliances and concluded that properly operated and ventilated appliances do not contribute significantly to indoor VOC levels.

Cooking has also been identified as a potential source of indoor VOCs. Sexton et al. (1986) found that frying hamburger emitted a variety of aldehydes, ketones, and amines. Clobes et al. (1992) continuously monitored VOC levels inside of a home, and reported that cooking can cause short-term increases in VOC concentrations.

2.1.3.3 Building Materials and Consumer Products

Building materials and consumer products are another potential source of VOCs in the indoor environment. Mølhave and Møller (1979) reported that the number and concentration of VOCs found in new Danish homes were greater than those found in older homes. The difference was attributed to lower ventilation rates and the presence of new VOC sources including building materials and furniture. Mølhave (1982) identified ten VOCs frequently observed in indoor environments and suggested that the major sources of the compounds were building materials, furnishings, and consumer products.

Lebret et al. (1986) studied 45 VOCs in over 300 Dutch homes and concluded that both building materials and consumer products were indoor sources of most of the VOCs studied. Noting the near ubiquitous presence of "solvent-type" compounds in homes in geographic regions where differing building materials are used, de Bortoli et al. (1986) pointed to the use of consumer products as an important source of VOCs indoors.

Seifert et al. (1989) followed VOC levels in 12 Berlin homes for a period of one year. Painting and other renovation activities resulted in increases in VOC concentrations by factors of 3 to 10. The study also found that elevated concentrations of specific VOCs could be linked to the use of products such as adhesives, felt markers, correction fluids, and cleaning agents. An earlier study found that extremely high levels of toluene in one



home could be attributed to the presence of a large number of freshly-printed newspapers and magazines (Seifert and Abraham, 1982).

Wallace et al. (1987b) performed headspace tests on 15 common building materials and consumer products including cleaning agents, waxes and polishes, carpet and wallpaper adhesives, carpets, ceiling tiles, sheetrock, and pesticides. Between 10 and 100 organic compounds were found to be off-gassing at detectable levels from each material. The authors concluded that nearly every home or business contains materials that may cause elevated exposures to toxic chemicals.

Tichenor and Mason (1988) examined the VOC emission characteristics of a variety of consumer products and building materials. They found that emissions rates vary with time, and can be vastly different depending on the compound. Table 2-4 lists representative compounds found in headspace analyses of a number of materials.

2.1.4 Personal Activities

One of the main results of the influential TEAM studies of the 1980s was the suggestion that many common activities, such as smoking, driving, pumping gas, and visiting the dry cleaners can result in increased levels of personal exposure to VOCs (Wallace, 1987a; Wallace et al., 1987c, 1988). Occupations such as chemicals or plastics processing, garage or repair work, and printing were also implicated in elevated levels of exposure (Wallace, 1987a; Wallace et al., 1987c).

The idea that human activities were a significant source of indoor VOCs certainly pre-dated the TEAM study. Johansson (1978) found that both the number and concentration of VOCs inside of two schoolrooms increased in the presence of humans.

Subsequent to the TEAM studies, Wallace et al. (1989) undertook a controlled study into the effects of 25 common activities on VOC concentrations in indoor air, and personal exposures to selected VOCs. The study identified some activities that resulted in very large increases in exposure to certain VOCs. Visiting the dry cleaners resulted in



Table 2-4 Compounds emitted by building materials and consumer products (Tichenor and Mason, 1988)

Material/Product	Major organic compounds identified
silicone caulk	metyhl ethyl ketone, butyl propionate, 2-butoxyethanol, butanol, benzene, toluene
floor adhesive	nonae, decane, undecane, dimethyloctane, 2-methylnonane, dimethylbenzene
particleboard	formaldehyde, acetone, hexanal, propanol, butanone, benzaldehyde, benzene
moth crystals	p-dichlorobenzene
floor wax	nonane, decane, undecane, dimethyloctane, trimethylcyclohexane. ethylmethylbenzene
wood stain	nonane, decane, undecane, methyloctane, dimethylnonane, trimethylbenzene
latex paint	2-propanol, butanone, ethylbenzene, propylbenzene, 1,1-oxybisbutane, butylpropionate, toluene
furniture polish	trimethylpentane, dimethylhexane, trimethylhexane, trimethylpentane, ethylbenzene, limonene
polyurethane floor finish	nonane, decane, undecane, butanone, ethylbenzene, dimethylbenzene
room freshener	nonane, decane, undecane, ethylpentane, limonene, substituted aromatics

greatly elevated exposures to trichloroethane and tetrachloroehylene. The use of room air deodorizers resulted in twofold increases in levels of p-dichlorobenzene. Painting and paint-related activities resulted in increasing 9-hour average concentrations of some aromatics and aliphatics by two orders of magnitude. Use of hot water for washing dishes or clothes resulted in elevated levels of chloroform. Hot showers were also identified as potentially dominant sources of chloroform exposure. Breath levels of styrene and benzene were 5-10 times higher in cigarette smokers than in nonsmokers or pipe and cigar smokers.

Clobes et al. (1992) used continuous monitors to evaluate the effect of human



activities on VOC levels in eight residences. Time-activity diaries allowed the investigators to link changing VOC levels with various activities. Activities such as cooking, cleaning, washing clothes, and painting were found to result in temporarily elevated levels of VOCs. After completion of the activity, VOC levels dropped off.

Opening a window, except in one case where leaves were being burned in a neighbor's yard, decreased VOC levels. VOC levels also decreased when air conditioners were operating.

2.1.5 Seasonal Variations

Concentrations of VOCs in outdoor, indoor, and personal air can vary from season to season. These differences have been attributed to a variety of factors such as meteorology, photochemical reactions, ventilation, and activity patterns.

Cheng et al. (1997) examined seasonal variations in VOC levels at two sites in Edmonton, AB. At the downtown site, distinct seasonal differences in VOC concentrations were observed, with total levels being highest in the winter and lowest in the summer. The difference was attributed to variations in meteorology. In particular, mixing heights are typically much lower in winter than in summer. No seasonal pattern was observed at the industrial site. The dominance of nearby industrial sources was identified as the reason for the lack of seasonal differences at the industrial site.

In a study of 12 Berlin households over a period of one year, indoor VOC levels were 2-3 times greater between November and April than between May and October (Seifert and Abraham, 1989). Reduced ventilation rates were identified as a potential explanation for the difference.

The 1987 TEAM study in Los Angeles, CA found increases in VOC concentrations in both outdoor and personal air during the winter (Hartwell et al., 1992). Eleven of eleven outdoor air medians were significantly higher in winter than in summer, as were nine of twelve personal air medians. The study identified the greater intensity of



photochemical reactions during the summer as a possible source of the difference.

Fellin and Otson (1994) examined the influence of climatic factors on VOC levels inside 754 Canadian residences. Mean summer concentrations were observed to be lower than other seasons. When outdoor temperatures exceeded 15 °C, mean VOC concentrations were found to be about half those found at lower temperatures. However, VOC concentrations were poorly correlated with outdoor temperatures and relative humidity. While the results were consistent with the expected seasonal variations in household ventilation, the presence of indoor VOC sources was more influential.

2.2 Exposure Assessment

Human exposure assessment is increasingly becoming an important tool in the identification and determination of the risks posed to public health by airborne pollutants. Historically, scientific and regulatory programs have focused on monitoring pollution concentrations at fixed outdoor locations or at specific pollutant sources. Since the late 1960s, there has been a growing recognition that the actual concentrations of pollutants to which humans are exposed may differ significantly from ambient concentrations at fixed sites (Cortese and Spengler, 1976; Spengler et al., 1979; Yocom, 1982; Spengler and Sexton, 1983; Spengler and Soczek, 1984; Ott, 1990).

Ott (1985) proposed a five-part conceptual model to describe the risk to public health posed by environmental pollutants. Determination of the human health risks associated with pollution requires knowledge of each of the five components of the risk model:

- the sources of environmental pollutants,
- the fate and transport of environmental pollutants,
- the exposure of humans to environmental pollutants,
- the dose received by exposed individuals, and
- the resulting health effects.



Each component of the model follows naturally from the preceding component, forming a five-link chain. Without knowledge of all five links, our overall picture of risk is incomplete, so knowledge of human exposure is essential to fully understand and manage environmental pollution risks. The report of the National Academy of Sciences (NAS) (1991) identified human exposure assessment as providing "fundamental information for describing the distribution (including high and low extremes) of contaminant exposures within a population for estimating doses received from different media, and for determining routes of entry into the body."

2.2.1 Defining Exposure

A variety of diverse definitions of exposure have appeared in the literature. Ott (1995a) recognized the need to establish a common, rational, quantitative definition of exposure. Zartarian et al. (1997) identified common ground amongst the many definitions of exposure: it predominantly involved contact between a target (human or otherwise) and an agent (physical, chemical, or biological).

The National Academy of Sciences (NAS, 1991) defined exposure as "an event that occurs when there is contact at a boundary between a human and the environment with a contaminant of a specific concentration for an interval of time; the units are concentration multiplied by time." This can be expressed mathematically by the equation (Lioy, 1990):

$$E = \int_{t_2}^{t_1} C(t) dt, \qquad (Eqn. 2-1)$$

where E is exposure, C(t) is concentration as a function of time, and dt is an increment of time from t_1 to t_2 . Ott (1995a) suggested that this definition was restrictive and described a specific type of exposure with respect to time – the "integrated exposure". He further suggested that a more fundamental definition was necessary. Williams (1995) argued that



the time resolution of the exposure should match that of the health effect being studied.

Ott (1982) proposed a statistical definition of exposure as the joint occurrence of two events: (1) the pollutant of concentration C is present at a particular location at a particular time, and (2) the person is present at the same time and location in space. This conceptual definition can be represented by the expression (Ott, 1995a):

$$\left\{
 \begin{array}{l}
 \text{Person i is present at} \\
 \text{Location}(x, y, z) \text{ at time } t
 \end{array}
\right\} \cap
 \left\{
 \begin{array}{l}
 \text{Concentration C is present at} \\
 \text{Location}(x, y, z) \text{ at time } t
 \end{array}
\right\}.$$
(Eqn. 2-2)

Recognizing that different parts of the target may receive different exposures simultaneously, Duan et al. (1989) proposed a more general definition as given by the expression:

From this fundamental definition of instantaneous point exposure, one can derive all other formulations of exposure with respect to space and time (Ott, 1995a).

Georgopolous and Lioy (1994) built upon this definition and presented it within a formal, conceptual, and mathematical framework for refining the characterization of human exposure and dose. Zartarian et al. (1997) developed a unified theoretical framework for understanding exposure to environmental pollutants. Within this framework, they defined the three basic components of exposure: a target, an agent, and contact. Additionally, they defined three essential concepts: contact boundary, contact zone, and concentration. The contact boundary is defined as "a surface in space containing at least one exposure point on the target of interest." Contact zone is defined as "a volume adjoining a contact boundary in which agent has a high probability of



contacting the contact boundary in the time interval of interest." Concentration at a point is given by the equation:

$$C(x_i, y_i, z_i, t) = \lim_{\Delta V_i \to 0} \left(\frac{\Delta m_i}{\Delta V_i} \right) = \frac{\mathrm{d}m}{\mathrm{d}V} , \qquad (\text{Eqn. 2-4})$$

where Δm_i is the mass of agent contained in the *i*th contact zone element, and ΔV_i is the volume of the *i*th contact zone element. From this framework, one can derive different formulations of exposure and apply them to various targets, agents, and media.

2.2.2 Measuring Exposure

Duan (1982) suggested the term "microenvironments" to describe the different locations (with different pollution concentrations) a human subject may pass through in the course of his or her daily activities. A microenvironment is further defined as a volume of air space with a homogeneous pollutant concentration. To study an individual's exposure to a pollutant, it is necessary that we keep track of all microenvironments through which they pass.

Within the microenvironmental framework, there are two basic approaches to studying human exposure: direct and indirect (Duan, 1982). The direct approach uses some form of personal exposure monitor (PEM) to measure exposure directly. With the indirect approach, microenvironmental pollutant concentration measurements are taken, and used in conjunction with time-activity data to reconstruct exposure.

Lioy (1995) identifies five basic direct and indirect tools for measuring or estimating exposure: (1) fixed site monitoring (indirect); (2) microenvironmental monitoring (indirect); (3) personal monitoring (direct); (4) survey instruments (indirect); and (5) exposure models (indirect). He also describes a hierarchy of exposure data with uncertainty decreasing as measurements are made progressively closer to the individual. Ott (1995a) emphasized the importance of a "receptor-oriented" approach to exposure assessment.



2.2.3 Indoor Air Monitoring

In describing the microenvironmental approach to estimating exposure, Duan (1982) stated that an individual's integrated exposure (E) is represented by the equation:

$$E = \sum_{k} c_k t_k , \qquad (Eqn. 2-5)$$

where c_k is the concentration of pollutant in the kth microenvironment, and t_k is the time spent in the kth microenvironment. From the equation, it is apparent that there are two factors that influence total exposure. To accurately estimate exposure, it is necessary to monitor those microenvironments where the pollutant concentration is very high, or where an individual spends a great deal of time.

Studies of human activity patterns have indicated that people spend a significant amount of their time indoors. Szalai (1972) and Chapin (1974) both reported that about 22 hours of each day are spent indoors, of which about 16 hours are spent inside the home. Leech et al. (1996) surveyed over 2,000 Canadians and found that, on average, respondents spent 89% of their time indoors, 66% of it inside their own homes. This implies that the measurement of pollutant concentrations in indoor air, and especially inside the home, is essential to the accurate estimation of human exposure. Yocom (1982) further pointed out that those most vulnerable to health risks from air pollution (infants, the elderly, and the infirm) often spend nearly 100% of their time indoors.

Numerous authors have suggested that fixed ambient monitoring is inadequate to represent personal exposure, and that greater attention be paid to indoor and personal monitoring (Yocom ,1982; Spengler and Sexton, 1983; Spengler and Soczek, 1984). Studies supporting this contention have been reported for a variety of air pollutants including carbon monoxide, sulfur dioxide, nitrogen dioxide, particulate matter, and VOCs (Binder et al., 1976; Cortese and Spengler, 1976; Spengler et al., 1979; Michael et al., 1990).



2.2.4 Personal Monitoring

While microenvironmental monitoring provides a better estimate of exposure than ambient monitoring, personal monitoring yields an even more accurate estimate (Mage, 1985; Lioy, 1995). This increase in accuracy is usually accompanied by an increase in cost and complexity of the study (Mage, 1985). There remains no substitute for field measurements in accurately determining exposure to air pollution (Wallace and Ott, 1982).

The development of various types of personal exposure monitors (PEMs) has made personal exposure monitoring more feasible. PEMs are small, lightweight instruments or devices that can be conveniently carried by people while they carry out their normal activities (Wallace and Ott, 1982). The convenience with which they can be carried is the characteristic that distinguishes PEMs from other types of portable monitors.

Tompkins et al. (1977) described desirable characteristics of a personal sampling device for use in industrial compliance monitoring. The device should:

- sample the breathing zone;
- collect a sample proportional to the time-weighted average concentration;
- provide an accurate measurement;
- cause minimal interference with the performance of job duties; and
- provide measurements at an acceptable cost.

There are two basic classes of personal monitors: analytical devices, which give instantaneous contaminant measurement; and collection (or integration) devices, which collect pollutant samples for later analysis (Wallace and Ott, 1982). Analytical devices have the advantage that concentrations are measured as a function of time, so exposure levels can be linked to specific events. Collection devices are limited to providing integrated measures of concentration over the entire sampling period, but the collected



samples may be subjected to more complex analysis in the laboratory than possible with an analytical sampler. Analytical devices are typically more complex and expensive than collection devices (Wallace and Ott, 1982).

The two basic classes of personal monitors can be further divided into two types: active and passive devices (Wallace and Ott, 1982). Active monitors use a pump to draw air across an analytical sensor or collector. Passive monitors use the principles of diffusion or permeation to bring the contaminant into contact with the collector. Active devices have the disadvantage of requiring a pump and power supply, which may be bulky and require some maintenance. Passive monitors are typically smaller, require little or no power, and are usually less expensive than their active counterparts. As passive monitors depend on diffusion, the sampling time required to collect analytically sufficient amounts of contaminant is typically longer than that for active samplers.

2.3 Passive Sampling

Passive sampling techniques rely on the principle of diffusion to collect contaminant molecules from the air without the use of a pump or other air-moving device (Rose and Perkins, 1982). For this reason, passive sampling is often referred to as diffusive sampling. As no pump is required, passive monitors are typically simpler, more compact, and lighter than active sampling monitors (Hill and Fraser, 1980). These characteristics make passive monitors ideally suited to personal monitoring of airborne pollutants (Coutant and Scott, 1982). They can be worn while a person undertakes their everyday activities with a minimum of inconvenience, or placed unobtrusively inside of a home.

2.3.1 Theory of Passive Sampling

Passive samplers typically consist of a liquid or solid sorbent separated from the ambient air by an air gap. The type of sorbent depends on the target analyte or analytes.



Activated carbon is commonly used in passive samplers designed to collect organic compounds.

Unlike active monitors, passive monitors rely on the diffusion of pollutant molecules across a stagnant air space (Rose and Perkins, 1982). The transport of contaminant to the sorbent is governed by Fick's First Law of Diffusion (Lautenberger et al., 1981):

$$J = -D\frac{\Delta c}{\Delta x},$$
 (Eqn. 2-6)

where J is the mass flux of the migrating contaminant, D is the diffusion coefficient of the contaminant, and $\Delta c/\Delta x$ is the contaminant concentration gradient across the air gap. The negative sign indicates the direction of mass transport from the higher concentration to the lower concentration.

The mass transfer rate is found by multiplying the mass flux by the crosssectional area yielding the equation:

$$\frac{M}{t} = -DA \frac{\Delta c}{\Delta r},$$
 (Eqn. 2-7)

where M is the mass of contaminant collected, t is the sampling time, and A is the cross-sectional area of the air space.

Assuming steady state conditions and a constant concentration gradient, the gradient is given by the change in concentration from the ambient air to the sorbent surface divided by the length of the diffusion path (see Figure 2-1)(Rose and Perkins, 1982):

$$\frac{\Delta c}{\Delta x} = \frac{C_A - C_0}{L}, \qquad (Eqn. 2-8)$$

where C_A is the contaminant concentration in ambient air, C_0 is the contaminant concentration at the sorbent surface, and L is the length of the diffusion path.



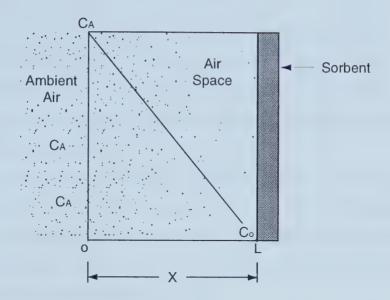


Figure 2-1 Fick's Law derivation for a passive sampler (after Lautenberger et al., 1981)

Further assuming that the sorbent is an efficient sink, the concentration at the sorbent surface is zero and gradient is given by (Lautenberger et al., 1981):

$$\frac{\Delta c}{\Delta x} = \frac{C_A}{L}.$$
 (Eqn. 2-9)

Substituting into the mass transfer equation (Eqn. 2-7) yields:

$$\frac{M}{t} = \left(\frac{DA}{L}\right)C_A,\tag{Eqn. 2-10}$$

The *DA/L* term is referred to as the sampling rate and is fixed by the diffusion coefficient of the contaminant and the geometry of the monitor. The sampling rate is computed or determined experimentally. Given the sampling rate, mass of contaminant collected, and the sampling time, the ambient air concentration is computed as:

$$C = \frac{M}{t \times samplingrate} \,. \tag{Eqn. 2-11}$$



2.3.2 OVM 3500

The passive sampler selected for use in this study was the 3M 3500 Organic Vapor Monitor (OVM 3500). The OVM 3500 is a commercially available sampling badge designed to measure average concentrations over a given time interval (3M, 1996a). Its primary use is in measuring occupational exposures to organic pollutants in industrial environments (3M, 1999).

The OVM 3500 consists of a single charcoal adsorbent pad contained within a circular plastic case (3M, 1999). A Teflon membrane held on by a plastic retaining ring covers the face of the sampler. A plastic spacer is used to maintain the air space between the membrane and the charcoal pad. A metal clip allows the sampler to be worn on a shirt collar or attached to an appropriate surface.

The samplers are received from the supplier inside a sealed evacuated metal can. Also inside each can is a plastic closure cap. To deploy the sampler, the can is opened and the sampler removed. Upon retrieval, the plastic retaining ring and membrane are removed and the closure cap is snapped on. More detailed procedures on field deployment of the samplers are included in Chapter 4.

2.3.3 Sources of Measurement Error

There are number of factors which may affect the performance of a passive monitor. Environmental factors such as temperature, relative humidity, face velocity, and concentration fluctuations may affect sampling accuracy. General information about these interferences, as well as specific information relevant to the OVM 3500 follow.

2.3.3.1 Temperature

The diffusion coefficient of a contaminant is proportional to absolute temperature raised to the three-halves power and inversely proportional to atmospheric pressure



(Tompkins and Goldsmith, 1977):

$$D\alpha \frac{T^{\frac{\gamma_{2}}{2}}}{P}$$
. (Eqn. 2-12)

With the sampler geometry essentially fixed, the sampling rate increases with temperature.

By the ideal gas law, the concentration of the contaminant is directly proportional to atmospheric pressure, and inversely proportional to absolute temperature (Lautenberger et al., 1981):

$$C\alpha \frac{P}{T}$$
. (Eqn. 2-13)

From equation 2-10, the mass of contaminant collected is proportional to the product of the diffusion coefficient and the ambient air concentration, so (Lautenberger et al., 1981):

$$M\alpha \frac{T^{\frac{3}{2}}}{P} \times \frac{P}{T}$$
. (Eqn. 2-14)

The result of this relationship is that the amount of contaminant collected is independent of the atmospheric pressure and proportional to the square root of absolute temperature. The implication of this result is that at a fixed concentration, a greater mass of contaminant will be collected at higher temperatures.

Changes in temperature can also affect the efficiency of the sorbent. The affinity of a sorbent for a chemical decreases with increasing temperature (Cheremisinoff and Ellerbusch, 1978; Guild et al., 1992). This counteracts the increase in sampling rate with temperature, and lessens the overall impact of temperature on sampler performance.

For its organic vapor monitors, 3M (1999) suggests a 1% correction factor for each 6°C above or below 25°C. Tang et al. (1993) examined sampling rates for the 3M OVM 3500 for styrene at varying temperatures and found that they increased with temperature. However, the variation was less than 10% within a temperature range of 10–



 36° C. Gagner (1996) examined the performance of the OVM 3500 at below zero temperatures, and concluded that the sampling rates did not decrease as predicted by diffusion theory, and that no correction factors were necessary down to -15° C. This was attributed to the effect of low temperatures on sorbent efficiency.

2.3.3.2 Relative Humidity

Relative humidity has also been identified as a potential source of interference for passive samplers (Coulson, 1981; Lautenberger et al., 1981). Increased relative humidity will decrease the affinity and the maximum capacity of the sorbent (Lautenberger ,1981). This can result in breakthrough, especially if the air concentration is high. Two humidity effects are described: modification of the sorbent surface by moisture, and competition for sorption sites by water vapor (Guild et al., 1992; Tang et al., 1993).

3M (1996b) found that sampling with the OVM 3500 in high humidity did not affect recovery coefficients for aliphatic, aromatic, and most halogenated hydrocarbons. Ketones and other double-bonded hydrocarbons were susceptible to storage losses and analysis should be expedited or samples stored in refrigerated conditions. Examinations of a number of compounds found no significant effects of humidity on the uptake rate of the badge (3M, 1996c, 1996d, 1996e).

Tang et al. (1993) examined the effect of humidity on the sampling rate of styrene for the OVM 3500. It was found that in the range of 20–90% relative humidity, the variation in sampling rate was less than 10%. Cohen et al. (1990) studied the performance of the OVM 3500 at varying concentrations and relative humidity. They found that accuracy was best at under two conditions: (1) low concentration ($10 \mu g/m^3$) and high relative humidity (75%); and (2) high concentration ($100 \mu g/m^3$) and low relative humidity (25%). Gagner (1996) found that while badge performance was affected by high humidity, the overall result was negligible.



2.3.3.3 Face Velocity

As passive samplers rely on diffusion processes, they are susceptible to starvation or depletion effects in stagnant air conditions (Lautenberger ,1981; Wallace and Ott, 1982). Tompkins and Goldsmith (1977) emphasized that to ensure accurate measurement, all resistance to contaminant transport should be contained within the stagnant air layer inside of the device. In stagnant air conditions, convective airflow across the face of the sampler may not be adequate to replenish pollutant concentrations in the boundary layer near the badge. This results in a local pollutant concentration at the badge face less than that of the bulk ambient air, essentially "starving" the badge and underestimating the actual concentration (Jonas et al., 1981; Wallace and Ott, 1982). Additionally, stagnant air at the face of the sampler results in a thicker boundary layer and effectively lengthens the diffusion path (Rose and Perkins, 1982; Harper and Purnell, 1987; Brown, 1993). To avoid starvation effects, a minimum face velocity of around 0.1 m/sec has been suggested (Tompkins and Goldsmith, 1977; Lautenberger et al., 1981).

Otson and Fellin (1991) tested several passive samplers over a range of face velocities from 0.01–1.8 m/sec, and found that the OVM 3500 performed well with only a slight increase in sampling rate. Similarly, Tang et al. (1993) tested the performance of the OVM 3500 over a range of face velocities, and found that the sampling rate of styrene increased only slightly with increased face velocity. It was also noted that the OVM 3500 performed well at a face velocity of 0.01 m/sec, well below the typically recommended minimum face velocity.

Hori and Tanaka (1996) examined the effects of face velocity on two types of passive samplers. The badges were exposed to a fixed concentration at various face velocities between 0 and 2.0 m/sec. The vapor concentration measured by the OVM 3500 was nearly the same (and close to the actual chamber concentrations) at face velocities between 0.5 and 2.0 m/sec. Only when the face velocity was reduced to zero did the



sampler significantly underestimate the chamber concentration. The second sampler demonstrated a clear increase in measured concentration with increased face velocity. The difference in performance between the two samplers was attributed to the membrane covering the face of the OVM 3500.

2.3.3.4 Fluctuating Concentrations

The application of Fick's first law of diffusion to passive sampling implies two assumptions: (1) the concentration gradient in the stagnant air gap reaches steady state conditions rapidly with respect to the overall sampling time, and (2) the concentration remains constant throughout the sampling period (Hearl and Manning, 1980).

Environmental conditions that satisfy these assumptions are seldom found in actual sampling situations: concentrations fluctuate over the course of a sampling period. Hearl and Manning (1980) analyzed the transient response of a passive monitor, developed a model to describe its behavior, and suggested a factor to correct concentration estimates. Bartley et al. (1983) presented a theoretical analysis of fluctuation-induced errors in a passive sampler with a single sorbent surface, and concluded that significant error can be present in estimates of averages of rapidly-varying concentrations. A sampler modification is suggested to reduce or eliminate this error. Bartley (1983) suggested the use of multiple sorbent surfaces to reduce the fluctuation-related error in time-weighted average concentrations determined by a passive sampler.

Contrary to these theoretical analyses, a number investigators have shown experimentally that transient vapor concentrations do not significantly affect sampler response (Einfeld, 1983; Compton et al., 1984; Hori and Tanaka, 1993). Compton et al. (1984) exposed three passive samplers to square wave concentration profiles with periods of two, six, and ten minutes. The concentration fluctuations did not significantly affect the time-weighted average concentrations given by two of the three samplers, including the OVM 3500. Hori and Tanaka (1993) presented theoretical and experimental results



suggesting that no correction factor was necessary.

2.3.4 Passive Sampling of Ambient Concentrations of VOCs

Most commercially-available passive sampling devices, such as the OVM 3500, were originally developed for use in the workplace. As such, the testing and validation of such devices has focused on the monitoring of relatively high pollutant concentrations which may be found in industrial settings. As interest in receptor-based approaches to exposure assessment grew, investigators looked towards passive sampling devices as convenient and inexpensive personal monitors for the lower concentrations found in ambient air.

Coutant and Scott (1982) performed one of the first evaluations of passive sampling devices in monitoring organic compounds in ambient air. Tests were performed on three commercially-available badges: the DuPont ProTek organic vapor air monitoring badge, the 3M OVM 3500, and the Abcor Gasbadge organic vapor dosimeter. Potential analytical problems were identified by examining detection limits, desorption efficiencies, and blank levels for each badge. For most of the eight compounds studied, blank levels on all badges were not only high, but highly variable. The uncertainty in background levels limits the practical use of the badges in sampling low concentrations of VOCs. Detection limits using conventional gas-chromatographic analysis were determined to be too high for the amounts of chemical likely to be collected over an 8-24 hour sampling period. Despite these limitations, it was felt that better quality control in the manufacturing process could result in lower and less variable blank levels, thereby improving the utility of the badges in monitoring ambient VOC concentrations. Coutant and Scott further note that such improvements in blank levels had been demonstrated subsequent to their testing.

Seifert and Abraham (1983) exposed Gasbadge samplers to test atmospheres with known concentrations of aliphatic and aromatic hydrocarbons ranging from 75 to 5,000



 $\mu g/m^3$. The samplers were found to be accurate, and that "the amount of substance trapped by the sampler is a linear function of the time of exposure." A detection limit of $300~\mu g \cdot h/m^3$ was reported.

Shields and Weschler (1987) tested 3M OVM 3500 samplers outdoors and inside several telephone offices in New Jersey, Wisconsin, and Missouri. Sampling periods ranged from two to eight weeks in length. During these periods, ambient concentrations ranged from $0.06~\mu g/m^3$ to $700~\mu g/m^3$. Analysis of 31-day triplicate samples found that for compounds with mean concentrations greater than $0.2~\mu g/m^3$, the average standard deviation was about 13% of the mean concentration. The results of the testing were consistent with the expected linear sampling behavior. At typical ambient concentrations badge capacities were not approached, even after eight weeks of exposure. A detection limit of $0.06~\mu g/m^3$ was reported for a four-week exposure. Shields and Weschler concluded that passive samplers are effective tools for monitoring low levels of VOCs over long time periods.

OVM 3500 samplers were tested for use in a study of VOCs inside of 12 German homes (Seifert and Abraham, 1989). Good agreement was observed between concentrations determined by the OVM 3500, the Gasbadge passive sampler, and a charcoal tube active sampling method. All of the methods showed acceptable agreement with the known concentrations of the test atmospheres.

Cohen et al. (1990) exposed OVM 3500 samplers for 21-days to test atmospheres containing two different concentrations (10 and 100 $\mu g/m^3$) of five VOCs at two relative humidities (25% and 75%). The results were compared to known concentrations and the concentrations as measured by an active sampling method. Under most conditions, the differences were less than 25%. Sampling of chloroform showed the least agreement with deviations of up to 80%. The best results occurred under conditions of high relative humidity/low concentration, and low relative humidity/high concentration.

As part of a Health and Welfare Canada program to develop suitable methods of



monitoring personal exposure to VOCs, five commercially-available passive sampling devices were examined (Otson, 1990). Of these five, two monitors – the DuPont ProTek G-AA and the 3M OVM 3500 – were tested extensively. The badges were exposed simultaneously for 24 hours to test atmospheres of varying concentration (10-5000 μ g/ m³), relative humidity (10-95%), temperature (10-35 °C), and face velocity (0.05-1.8 m/ s). The ProTek badge showed greater variability under changing conditions, so only the OVM 3500 was evaluated for all 26 target compounds. The results obtained for the OVM 3500 showed good agreement with an active reference method. Replicate analysis found that the OVM 3500 showed better precision than the reference method. Method detection limits of 1- 2 μ g/m³ for a 24-hour sample were reported. Converted to a similar sampling period , this value is comparable to the value reported by Shields and Weschler (1987).

Otson et al. (1992a) performed further field testing on the OVM 3500. Samplers were placed in 17 homes and 1 office during the summer and in 4 homes the following winter. Outdoor samples were also taken during winter. Sampling times ranged from 48-96 hours in the summer, and 23-27 hours in the winter. Collocated active samplers were placed in some homes as a reference method. The concentration determined using the OVM 3500 showed excellent correlation with the reference method. Again, the precision of the passive sampler was slightly higher than the active reference method. Method detection limits around 2 μ g/m³ for a 24-hour exposure period were reported. The authors concluded that the passive method was convenient and inexpensive as compared to the active method.

2.4 Exposure to VOCs – Field Studies

2.4.1 Indoor-Outdoor Relationships

Interest in indoor air pollution began to grow in the late 1970s, and it is at this time that studies of the occurrence of VOCs in indoor air began to appear. Based on these



studies, several conclusions become evident:

- (1) indoor concentrations of most VOCs are typically greater than outdoor levels:
- (2) the variety of VOCs present at detectable levels is greater indoor than outdoors;
- (3) indoor VOC concentrations can vary by several orders of magnitude; and
- (4) indoor sources include building materials, consumer products, cigarettes, and gasoline.

Johansson (1978) examined the concentrations of fifteen VOCs inside of two schoolrooms in Stockholm, Sweden. Both the number of compounds detected and the concentration of VOCs were greater in indoor air than outdoor air. Similar conclusions were reported for a study of homes in the Chicago, Illinois area (Jarke et al., 1981; Becker, 1981). Johansson (1978) also reported that both the number and concentration of VOCs in indoor air increased in the presence of humans. Mølhave and Møller (1981) measured VOC concentrations in 39 Danish residences and found that indoor air concentrations typically exceeded corresponding outdoor air standards.

Contrary to the aforementioned studies, benzene levels inside of 15 Berlin residences were found to be lower than levels taken just outside of the dwellings (Seifert and Abraham, 1982). This study also found that toluene levels were higher indoors than outdoors and levels of ethylbenzene and xylenes were similar indoors and outdoors.

Measurements of benzene, toluene, and xylenes at a Berlin traffic intersection were found to be higher than concentrations found both indoors and outdoors. This may have been indicative of the impact of heavy traffic on concentrations at the intersection.

Lebret et al. (1986) measured the concentrations of 45 VOCs inside and outside of more than 300 Dutch homes. For nearly all of the compounds studied, indoor concentrations were found to be higher than those found outdoors. Some VOCs were observed to have relatively stable indoor concentrations, and such levels were attributed to constant indoor sources such as building materials. Other VOCs were found to vary widely, indicating that activities inside the home, such as the use of consumer products,



were important determinants of concentration.

Similar conclusions about consumer products as important indoor VOC sources were drawn based on a study of 35 VOCs in fourteen homes in northern Italy (De Bortoli et al., 1986). As in the Dutch study, indoor concentrations of nearly all of the VOCs studied were higher than those found outdoors. Many of the pollutants detected in the study were identified as "solvent type" compounds. These compounds occurred in both old and new homes, and have also been identified in homes in other studies in Europe and the US As building materials vary across geographic areas, the investigators suggested that the use of common consumer products was an important source of VOCs indoors.

The US EPA TEAM studies of the early and mid-1980s measured VOC levels indoors and outdoors in a variety of communities across the United States (Wallace, 1987a). The results of these studies indicated that for a majority of chemicals, indoor median and maximum VOC concentrations were higher than those found outdoors regardless of geographical area or season (Pellizzari et al., 1986). In some cases, median indoor/outdoor ratios exceeded 10.

A follow-up TEAM study was undertaken in 1987 in the Los Angeles, CA area (Hartwell et al., 1992). The study confirmed that indoor levels were much higher than the corresponding outdoor concentrations for most of the 22 VOCs studied. The distribution of VOCs throughout the home was also studied. Levels of VOCs in the kitchens of the homes were similar to those found in the primary living areas.

A study of homes in eastern Germany found a similar relationship between VOC concentrations in kitchens and living rooms (Schneider et al., 1999). While kitchen and living room levels were similar, both were typically higher than concentrations found in bedrooms. The study also found that while indoor VOC levels tended to increase with measurement height, the differences were not statistically significant.

Cohen et al. (1989) measured indoor and outdoor concentrations of VOCs in the



heavily industrialized Kanawha Valley region of West Virginia as part of a study into the impacts of the chemical industry on human exposure to VOCs. The region was chosen because industrial activity, traffic in the valley, topography, and meteorology in the region create the potential for high VOC concentrations. Three-week integrated indoor and outdoor VOC samples were collected at 31 homes in the valley and 4 homes out of the valley using the OVM 3500 passive sampler. Questionnaires regarding household characteristics and source use were administered. The results indicated that indoor concentrations were higher than outdoor concentrations. Outdoor levels of all but one compound were below detection limits for a majority of samples. Based on the sampling and questionnaire results, the investigators concluded that indoor sources were more important than outdoor sources. No differences between regions were identified.

A national pilot study on the occurrence of VOCs in Canadian residences was undertaken in 1991-92 (Otson et al., 1992b). A multi-stage stratified sampling design was used to select 757 homes from across Canada. A passive sampling device (OVM 3500) was placed in each home for a 24-hour period. Field measurements of temperature and relative humidity were made both indoors and outdoors. Air exchange rates were determined in 23 homes. Questionnaires on household characteristics and activities were administered in addition to the field measurements. The badges were initially analyzed for 26 VOCs. Subsequent analysis brought the total of identified compounds to 40 (Otson et al., 1994). Further retrospective analysis identified 52 additional compounds for a total of 92 VOCs identified in the samples (Otson, 1996).

2.4.2 Personal Exposure Studies

Studies of VOCs in personal air are fewer in number than those of indoor and outdoor air. The small number of studies is likely due to the increased complexity and cost of such studies, and the greater burden imposed on the participants.



2.4.2.1 Total Exposure Assessment Methodology (TEAM) Study

The US EPA Total Exposure Assessment Methodology (TEAM) study was carried out between 1979 and 1985. The objectives of the study were: (1) to develop methods to measure individual total exposure and resulting body burden of toxic and carcinogenic organic chemicals; and (2) to apply these methods to estimate the exposures and body burdens of urban populations in several US cities (Wallace, 1987b). To achieve these goals, a small personal sampler was developed, and a three-stage stratified probability sampling approach was adopted. The results of the study were detailed in a four-volume report (Wallace, 1987a) and numerous journal articles (Wallace et al., 1984, 1985, 1986, 1987a, b, 1988; Hartwell et al., 1987a, b).

The study was carried out in three phases. Phase I was a pilot study involving nine subjects in Bayonne and Elizabeth, New Jersey; and three subjects in North Carolina (Wallace et al., 1984). The second phase involved 350 persons in Bayonne and Elizabeth, New Jersey: cities with extensive chemical manufacturing and petroleum refining industries (Wallace et al., 1985, 1986). Samples were also taken for 25 persons in Greensboro, North Carolina; and 25 persons in Devils Lake, North Dakota (Wallace et al., 1987c). Greensboro is a city without major chemical manufacturing and petroleum refining activities, and Devils Lake is a small, rural and agricultural town far from the influence of major industry. Phase III involved 200 persons in Los Angeles, Antioch, and Pittsburg, California (Hartwell et al., 1987b; Wallace et al., 1988). These communities were selected due to the presence of petroleum refining and other industries. The main study was completed in 1985, and follow-up studies were carried out in 1987 and 1988 in Los Angeles, California; Baltimore, Maryland; and Bayonne and Elizabeth, New Jersey (Wallace, 1992).

Air samples were collected using an active sampling device consisting of a pump drawing air through a bed of Tenax GC encased in a glass tube. Each participant in the



various phases of the study carried a personal air sampler for two consecutive 12-hour periods. Similar samplers were deployed outside of some homes to collect daytime and overnight outdoor samples. Drinking water samples were collected twice a day, and each participant gave a breath sample at the end of the 24-hour period.

Air samples were analyzed by GC/MS for twenty target compounds. The target compounds were selected based on their extensive use, and likely toxicity. In addition to the personal and outdoor air sampling results, questionnaires were used to gather information about household characteristics and personal activities during the sampling period. Major findings of the TEAM study include (Wallace, 1987b):

- mean personal air exposures were greater than mean outdoor concentrations at
 7 of 8 locations;
- elevated indoor concentrations at home and at work were a major reason for the elevated personal concentrations;
- sources of VOCs in indoor air included consumer products, building materials, and personal activities such as smoking and pumping gas;
- breath levels of most chemicals were significantly correlated with personal air exposures, but not correlated with outdoor air concentrations;
- some specific sources of VOC exposure were identified including smoking,
 visiting the dry cleaner, pumping gas, and occupational exposures;
- local VOC sources were far more influential on total exposure than major
 point sources (industrial emissions) or area sources (visiting the dry cleaners
 or service station; and
- inhalation was the dominant exposure pathway for all of the target compounds except for trihalomethanes which were predominantly found in chlorinated drinking water.



2.4.2.2 German Environmental Study 1990/92 (GerES II)

The 1990-92 German Environmental Study (GerES II) was a large-scale study of the exposure of the German population to a variety of environmental pollutants including VOCs (Seifert et al., 2000). A two-stage stratified probability sampling design was used to select a sample of 2,524 German adults, from which a subsample of 113 subjects was selected for personal air monitoring of VOCs (Hoffmann et al., 2000).

Personal air samples were collected using the 3M OVM 3500 diffusive sampler. The samplers were worn for a seven-day period. Samples were analyzed using gas chromatography for 74 target compounds. A comparison of the GerES II results with the Fort McKay results is included in Chapter 6. Participants also completed detailed questionnaires regarding household and lifestyle characteristics. Time-activity data were also gathered using time-activity diary.

The results of the GerES II confirmed that passive sampling was a suitable technique for measuring personal exposure to VOCs (Hoffmann et al., 2000). In conjunction with time-activity information, such measurements can be used to estimate population distributions of VOCs. The results also indicated that personal exposures to aromatic VOCs were largely influenced by individual activities, especially smoking, automobile-related activities, and occupational exposures.

2.4.2.3 National Human Exposure Assessment Survey (NHEXAS)

As a preliminary field test for the US EPA's National Human Exposure

Assessment Survey (NHEXAS), measurements of VOCs in personal, indoor, and outdoor air were made in EPA Region V (the states of Minnesota, Wisconsin, Michigan, Illinois, Indiana, and Ohio) between July 1995 and May 1997 (Whitmore et al., 1999). The study used a four-stage stratified probability-based sampling design to select about 250 participants for the study.

Personal, indoor, and outdoor air VOC levels were monitored for a six day period



at each home (Clayton et al., 1999). One or two follow-up visits with lag times between one and eight months were made to around 100 homes.

Clayton et al. (1999) analyzed the results for four VOCs: benzene, chloroform, tetrachloroethylene (PERC), and trichloroethylene (TCE). Distributions of all four chemicals in personal, indoor, and outdoor air were observed to be right-skewed. Blood levels of VOCs were correlated with levels in personal air. Personal levels of benzene, PERC, and TCE exceeded levels found indoors and outdoors. Concentrations of all four chemicals in personal air were strongly correlated with indoor air levels. Personal air levels of all compounds except benzene were correlated with outdoor air levels. Benzene levels in personal air were heavily associated with smoking-related activities. The presence of a few extremely high personal exposures suggested occupational exposures to some of the chemicals

Analysis of longitudinal data from the follow-up visits indicated that temporal variations were greater than the variations between study participants. This seems to indicate that long-term exposures may not be adequately represented by just one or two six-day exposure periods. This is due, in part, to the fact that total exposure is influenced by activities that may be performed only occasionally.

2.4.3 Study Design Considerations

Laboratory and field studies have shown that passive sampling is an appropriate technique for measuring VOC concentrations in ambient air (Shields and Weschler, 1987; Cohen et al., 1989, 1990; Otson et al., 1992a, b, 1994). In particular, these studies have also demonstrated that the 3M OVM 3500 is a useful instrument for measuring VOC levels in indoor, outdoor, and personal air.

Review of previous studies of VOC concentrations in personal and indoor air reveals two basic hallmarks of such studies: (1) the use of a probability-based sampling method to select a representative sample; and (2) the use of questionnaires and time-



activity diaries to collect ancillary information related to exposure.

Probability-based samples are frequently used in population studies of VOCs in personal (Wallace, 1987a; Whitmore et al., 2000; Seifert et al., 2000) and indoor air (Otson et al., 1992b). Large-scale studies often employ stratified designs to select representative samples. In addition to helping to ensure a representative sample, probability-based sampling provides a scientifically-defensible basis for statistical inference and extrapolation from the sample to the whole population.

Nearly all of the studies of VOCs in personal and indoor air utilize some form of questionnaire to gather information about household characteristics and activities that may influence VOC levels. This information is important to identify potential sources of exposure. When personal monitoring is employed, diaries are often employed to provide detailed information about personal activities and the time spent in various microenvironments.



Chapter 3: Sample Selection Procedures

3.1 Sampling Design

3.1.1 Probability Sampling

The primary objective of this study was to obtain baseline exposure measurements which can be compared in a meaningful way to measurements made at some point in the future. Secondary objectives of this study included drawing inferences from the sample about the target population. A probability sample provides a defensible, quantifiable basis for making such inferences as are necessary to meet the study objectives. In probability sampling every item in the sampling frame has a known, non-zero probability of being selected for the sample (Cox et al., 1988).

The primary objective of a sampling procedure is to obtain a sample which closely represents the characteristics of the population as a whole (Yates, 1960). To help achieve this, procedures are designed to minimize the amount of bias in the sample. By definition, a probability sample is free from bias arising from sample selection and provides a more "credible" representation of the population than a haphazard selection procedure (Yates, 1960; Cochran, 1963; Stuart, 1984). For these reasons, a probability sampling design was developed for this study.

3.1.2 Stratification

Stratification involves division of the population into several sub-populations or strata, and the selection of independent samples from each. This has two basic results. First, the accuracy of the population estimates increases, especially if the variances within the strata are small. Second, stratification helps ensure that sections of the population that are of particular interest are adequately represented in the sample (Yates, 1960). Stratified sampling designs are commonly used in studies of population exposure to VOCs and other airborne pollutants (Wallace, 1987; Otson et al., 1992; Seifert et al., 2000).



For this study, a single stage stratification scheme was employed. The population was divided into two strata based on housing type: single-family detached houses, and mobile homes (trailers). From these two strata, independent random samples were selected from each. There were several reasons for using a stratified sampling scheme rather than a simple random sample. It was felt that the different ventilation characteristics of houses and mobile homes – mobile homes are typically tighter than houses – might have an impact on VOC concentrations within the home (Spengler and Sexton, 1983). Additionally, a large number of the mobile homes are clustered in one area of Fort McKay, so the stratification also has the result of helping to ensure geographic representativeness.

3.2 Sample Selection

3.2.1 Target Population

The target population for the study consisted of all occupied single-family housing units in the community of Fort McKay. As the focus of the study was on human exposure to VOCs and included measurements of VOC levels in personal air, unoccupied homes were excluded. For the personal air measurements, participation was restricted to residents over the age of eighteen.

3.2.2 Sampling Frame

The sampling frame was constructed from a housing list and map provided by the Fort McKay Industrial Relations Corporation (see Appendix 1). The completeness and accuracy of the housing list and map were verified by field staff in Fort McKay prior to sample selection. The housing list identified each home by number and housing type.

Based on the housing list, two sampling frames were constructed – one for each stratum. The Houses list consisted of 89 units, and the Mobile Home list consisted of 40 units.



3.2.3 Sample and Strata Sizes

The Central Limit Theorem states that as sample size increases, the distribution of the sampling average will approach the normal distribution. It is on this foundation that much of the scientific basis for statistical inference rests. It is important to ensure that a sample is large enough to yield an adequate approximation of the normal distribution. A sample size of 30 is usually considered adequate (Stuart, 1984). As such, a minimum sample size of 30 housing units was selected for this study.

The stratum sample sizes were based on the overall sample size and a uniform sampling fraction. The use of a variable sampling fraction can result in larger increases in the accuracy of population estimates by over-sampling the more variable strata. However, to achieve such increases, knowledge of the variance within each stratum is necessary (Stuart, 1984). For this study, the stratum variances were not known, so a uniform sampling fraction was used.

The use of a uniform sampling fraction means that stratum sample sizes are proportional to overall stratum size. Furthermore, all of the stratum weights will be equal, and the sample is considered self-weighting (Stuart, 1984). The self-weighting nature of the sample simplifies any statistical computations, as no consideration of stratum weights is necessary.

Based on an overall sample size of 30 and a uniform sampling fraction equal to 0.233, the sample sizes for the Houses and Mobile Homes strata were determined to be 21 and 9 units, respectively. As shown in Table 3-1, the working sampling fractions for each stratum differ slightly from the overall sampling fraction. These differences are negligible and did not have any practical impact on the results (Yates, 1960).



Table 3-1 Working stratum sampling fractions

Stratum	Population Sample Size		Sampling Fraction		
Houses	89	21	0.236		
Mobile Homes	40	9	0.225		
Total	129	30	0.233		

3.2.4 Random Selection Procedures

The housing units in each stratum were listed in order by house number and the lists numbered sequentially from one. The elements of the Houses stratum were numbered from 1 to 89. For the Mobile Homes stratum, the units were numbered from 1 to 40. Sample selections for each stratum were made separately and independently.

For the Houses stratum, two-digit random numbers were drawn from a table of random numbers (Yates, 1960). If the number did not fall between 1 and 89, it was disregarded and another number drawn. The house number corresponding to the selected random number was recorded. If the number drawn had previously been selected, it was discarded and another number selected. This process was repeated until a list of 45 houses had been selected.

A similar process was followed for the Mobile Homes stratum. Numbers not falling between 1 and 80 were discarded, as were previously selected numbers. Numbers between 41 and 80 were converted to numbers between 1 and 40 by subtracting 40 from the original number. The house number of the mobile home corresponding to the selected random number was recorded and the process repeated until a list of 25 mobile homes was generated.



3.3 Participant Recruitment

3.3.1 Recruitment Procedures

Using the randomly-selected lists, a door-to-door campaign was employed to recruit study participants. Prior to the recruitment phase, an informational letter (see Appendix 2) was circulated to all households indicating that the study was being undertaken and that they may be asked to participate.

The door-to-door campaign occurred over a two-week period one month prior to the scheduled starting date of the study. Field staff were dispatched to visit the selected homes beginning at the top of the list. During the visit, field staff further explained the study and answered any questions the resident may have had. If the residents had any questions that the recruiter could not answer, they were directed to contact the study coordinator. If the residents were willing to participate in the study, tentative sampling appointments were scheduled.

If no one was home at the time of the visit, field staff were instructed to make a minimum of three return visits to the home, or until a positive or negative response had been obtained. Once a positive or negative response had been obtained at a home, the recruiter moved to the next home on the list. The process continued until the desired number of houses and mobile homes were identified as willing participants.

3.3.2 Response Rates

The desired sample size was 21 houses and 9 mobile homes. Due to an administrative error, 20 houses and 10 mobile homes were selected for the fall sampling season. One of the mobile home residents declined to participate in the winter phase of the study, so an additional house was added to the study from the sample list. Response rates for the fall and winter sampling periods are summarized in Table 3-2. Numbers for the winter season include the fall recruitment and the additional participant recruited for



the winter.

Table 3-2 Response rates, fall and winter sampling seasons

	Houses		Mobile Homes		Overall	
	Fall	Winter	Fall	Winter	Fall	Winter
Total households approached	35	36	24	24	59	60
Consent received	21	21	10	9	31	30
Declined/Not at Home	14	15	14	15	28	30
Withdrew prior to study	1				1	0
Withdrew after fall sampling			1		1	0
Completed	20	21	10	9	30	30
Response rate	57%	58%	42%	38%	51%	50%



Chapter 4: Sample Collection

4.1 VOC Measurements

4.1.1 Equipment

4.1.1.1 OVM 3500

The passive monitor used in the study was the 3M 3500 organic vapor monitor (OVM 3500). Although the OVM 3500 was developed for industrial hygiene applications, several validation studies have been undertaken to support its use in monitoring ambient concentrations of VOCs (Coutant and Scott, 1982; Shields and Weschler, 1987; Seifert and Abraham, 1989; Cohen et al., 1990; Otson, 1990; Otson et al., 1992). Gagner (1996) performed validation studies of the OVM 3500 at temperatures down to –30 °C. It has also been used in numerous small-scale (Seifert and Abraham, 1989; Cohen et al., 1990) and large-scale (Otson et al., 1994; Gordon et al., 1999; Hoffmann et al., 2000) studies of VOCs in personal, indoor, and outdoor air. The results of the validation and field studies are detailed in the literature review.

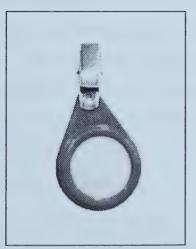


Figure 4-1 OVM 3500

The OVM 3500 is pictured in Figure 4-1. The badge consists of an orange plastic case containing a charcoal sorbent pad. A plastic spacer separates the pad from a Teflon membrane held on by a plastic retaining ring. The metal clip allows the badge to be affixed to a shirt collar or other appropriate surface. Each badge is shipped in an evacuated sealed aluminum can with a plastic snap lid. Along with the badge, each can contains a plastic elution or closure cap with two sealable ports.



4.1.1.2 Sampling Stands

Two types of sampling stands were used to hold the sampling badges at the desired sampling height of 1.2 m. The indoor sampling stands (pictured in Figure 4-2) were constructed from lengths of 3/4" PVC irrigation pipe. A T-shaped upright was screwed into a base. The samplers were attached to a length of cord suspended across the horizontal crosspiece. Short lengths of plastic tubing were used as spacers when duplicate or triplicate samplers were deployed.

During the fall sampling season, the PVC stands were also used outdoors with two modifications. The upright was attached to a broader base that was then pegged to the ground to prevent the stand from toppling over in the wind. Galvanized tin shelters were secured to the crossbeam to protect the outdoor samplers from precipitation and high winds.

During the winter sampling period, a wooden sampling stand (pictured in Figure 4-3) was used. The stand consisted of a central post to which four angled legs were bolted to provide a stable base even in deep snow. The samplers were affixed to a length of wire secured to the top of the post. An aluminum can was attached to the top of the post to provide shelter for the sampler.

Personal samplers were worn on the participant's shirt collar or worn on a cord around the neck as shown in Figure 4-4. The intention was to give the participant a convenient means of wearing the sampler while keeping it as close to the breathing zone as possible.

4.1.2 Sampling Location

In order to ensure representative samples, some general guidelines were followed in selecting the locations for the placement of the samplers. The guidelines were based on the manufacturer's recommendations (3M, 1999) and experiences from previous studies (Alberta Health, 2000a; Byrne, 2000). The intention of the guidelines was to locate the



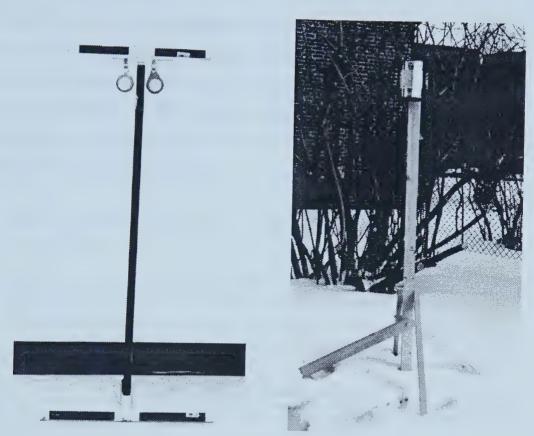


Figure 4-2 Indoor sampling stand

Figure 4-3 Outdoor sampling stand



Figure 4-4 Personal VOC sampler



sampler in an area of adequate air flow away from potential interference. Participants in the personal sampling portion of the study were also given guidelines for wearing the sampler. Guidelines for the placement of indoor, outdoor, and personal samplers are given in Table 4-1. While every effort was made to follow the guidelines, space restrictions sometimes prevented this. Location of indoor and outdoor samplers were noted on a floor plan, and the proximity to potential biases recorded.

Table 4-1 Guidelines for the placement of indoor, outdoor, and personal samplers

Indoor sampling location guidelines

- → place the sampler in the primary living space of the home;
- → place the sampler at least 2 m from exterior doors, windows and registers; and
- → avoid placing the sampler in a corner or along an exterior wall.

Outdoor sampling location guidelines

- → place the sampler in the yard away from the house or any other structures;
- → place the sampler at least 1 m from any tree or bush;
- → place the sampler at least 5 m from a driveway; and
- \rightarrow place the sampler at least 5 m from any exhaust vent (dryer, A/C, etc.).

Personal sampling guidelines

- \rightarrow handle the sampler by the clip only, do not touch the face of the sampler;
- → wear the sampler as close to the breathing zone as possible;
- → wear the sampler with the white membrane facing outwards;
- \rightarrow wear the sampler on the outside of all clothes, so that it is exposed to the air;
- → remove the sampler while sleeping; place the sampler on a table or nightstand in the bedroom;
- → keep the sampler dry; remove the sampler while showering or bathing; place the sampler on a counter or vanity in the bathroom; and
- → remove the sampler during activities, such as contact sports, where it may be damaged; leave the sampler in the area where the activity is taking place.



4.1.3 Sampling Protocols

Each sampler was deployed and terminated following the protocols outlined below. Procedures were based on the manufacturer's recommendations (3M, 1999). Protocols for sample deployment and termination are given in Tables 4-2 and 4-3 respectively.

Table 4-2 Sample deployment procedures

- 1. Select sampling locations based on appropriate guidelines. Set up sampling stand.
- 2. Remove plastic lid from the sampler can. Check that the labels under the ring match those on the outside of the can and lid.
- 3. Open the container by lifting the ring tab and carefully pulling it back. Remove the VOC sampler without touching the white membrane. Replace the plastic lid on the can
- 4. Place one label on the back of the sampler and another in the appropriate space on the field data log sheet.
- 5. Record the time and date of sample deployment on the log sheet.
- 6. Attach sampler to sampling stand or personal sampling participant using the metal clip. Ensure that the membrane is facing outwards.
- 7. Repeat above procedures for duplicate or triplicate samples.

Table 4-3 Sample termination procedures

- 1. Retrieve the appropriate sampler can. Remove the plastic lid from the can, and extract the plastic closure cap. Ensure that the port plugs are firmly seated.
- 2. Detach sampler from sampling stand. Verify that the label on the back of the sampler match those on the can and lid.
- 3. Remove the plastic retaining ring, prying it off with a coin if necessary. Place the ring and membrane into the empty can.
- 4. Quickly snap the closure cap onto the body of the sampler. Ensure that it is secure. Place the sealed sampler back into the can.
- 5. Record the date and time of sample termination on the field log sheet.
- 6. Replace the plastic lid on the can, and seal the can with parafilm.
- 7. Return sealed can to field office to await shipping.



About 10% of all samples were field blanks. All field blanks were deployed at the scheduled sampling location. Procedures for the deployment of field blanks are given in Table 4-4.

Table 4-4 Blank deployment procedures

- 1. Remove plastic lid from the sampler can. Check that the labels under the ring match those on the outside of the can and lid.
- 2. Open the container by lifting the ring tab and carefully pulling it back. Remove the VOC sampler without touching the white membrane.
- 3. Immediately remove the retaining ring and membrane, and snap the closure cap onto the body of the sampler. Ensure that the port plugs are firmly seated, and that the closure cap is secured to the sampler body.
- 4. Place one label on the back of the sampler and another in the appropriate space on the field data log sheet. Record the time and date of sample deployment on the log sheet.
- 5. Return the sampler to the can. Replace the lid and seal the can with parafilm.
- 6. Return the sealed can to the field office to await shipping
- 7. Return sealed can to field office to await shipping.

4.2 Air Exchange Measurements

During the fall sampling season, air exchange measurements were carried out using a method based on the perfluorocarbon technique described by Dietz and Cote (1982). Procedures, equipment and analysis services for the air exchange measurements were provided by Robert Weker at the Harvard School of Public Health (HSPH). A copy of the field protocol and laboratory methods is included in Appendix 3.

To find the average air exchange rate in a house, sources containing an inert, non-toxic tracer chemical, perfluorinated methylcyclohexane (PMCH), were deployed throughout the home. Within 24 hours, the PMCH reaches a steady-state concentration inside the home based the permeation rate of the PMCH sources, the house volume and temperature, and the air exchange rate. The PMCH concentration was measured using passive sampling devices called capillary adsorption tubes (CATs). The CATs were placed



in the home for a fixed period of time, and then returned to the laboratory for analysis. Subsequent to the removal of the CATs, the sources were removed and returned to the laboratory at HSPH for post-experimental permeation rate verification.

The amount of PMCH collected by each CAT was determined through gas chromatography. Based on these results, the air exchange rate (AER) was determined by the following equation:

$$AER = \frac{N \times R_{PERM} \times R_{CAT} \times T_{CAT}}{V_{PMCH} \times V_{HOUSE}},$$
 (Eqn. 4-1)

where N is the number of PMCH sources, R_{PERM} is the PMCH source permeation source rate, R_{CAT} is the CAT collection rate, T_{CAT} is the CAT exposure time, V_{PMCH} is the volume of PMCH found on the CAT, and V_{HOUSE} is the volume of the house.

4.2.1 Equipment

4.2.1.1 PMCH Sources

The PMCH sources consist of a 22-mm aluminum bullet shell impregnated with a solution of PMCH. The shell was encased in a $5 \text{ cm} \times 3 \text{ cm} \times 2 \text{ cm}$ piece of polyurethane foam. A numbered label is affixed to the source using a piece of adhesive tape. A hole was bored through the foam so that the source may be suspended by a length of string. Sources were shipped in a resealable plastic bag.

4.2.1.2 CATs

The CATs consisted of a 6.35 cm length of galls tubing (0.6 cm o.d., 0.4 cm i.d.) containing a small amount of a carbonized adsorbing material. The adsorbent was sandwiched between two stainless steel screens. Both ends of the tube were closed with plastic caps. A number was etched onto one end of the tube. CATs were shipped in groups of five inside small resealable plastics bags. Each bag contained some charcoal or carbon



paper to help protect the CATs from contamination.

4.2.2 Air Exchange Measurement Procedures

4.2.2.1 Locating Sources and CATs

Approximately one PMCH source is required for every 750 square feet or 75 m² of floor area. To determine the average air exchange rate of a home, as few as one or two CATs may be required.

Both sources and CATs should be placed at breathing height in areas with free movement of air. Sources must be placed where the tracer can be transported to all areas of the home. CATs and sources should be located away from doors and windows with strong drafts, stairways, and corners with restricted air movement. Sources of heat or cold should also be avoided. CATs should be placed away from refrigerators and dehumidifiers which contain freons which may interfere with the analysis. CATs should be placed at least 2 m from any PMCH source.

4.2.2.2 Field Procedures

To reduce the risk of contamination, sources and CATs should never be transported or shipped together. If they are to be transported in one vehicle, the sources should be kept in the trunk and the CATs in the passenger compartment of the vehicle. Both sources and CATs should be transported in resealable plastic bags containing charcoal or carbon paper.

The air exchange measurements required three visits to each home. On the first visit, only the sources were deployed. Following the guidelines for locating sources, they were taped in place or suspended by a length of string or dental floss. The source ID number, deployment date and time, and the source location were recorded on a log sheet. The locations were noted on the floor plan.

The CATs were deployed 24 hours after the first visit. Once the sampling



locations were identified, the CATs were removed from their plastic bag and secured in place with adhesive tape, or a wire or plastic tie. CATs can also be suspended in place by a length of wire or dental floss. CATs may be suspended vertically with the numbered end down, or placed on a flat surface with the numbered end protruding beyond the edge of the surface. The CAT was activated by removing the plastic cap on the numbered end of the tube. The CAT ID number, activation date and time, and sampling location were recorded on the log sheet and floor plan.

The third visit occurred 72 hours after the CATs were activated. The CATs were closed by replacing the plastic cap and returning them to their resealable bag. The date and time of closure were recorded on the log sheet. Exposed CATs were returned to the field office to await shipping to the HSPH analytical lab.

If possible, the PMCH sources should be left in place for an additional 24 hours. Otherwise, the CATs should be removed from the home first followed by the sources. Sources and exposed CATs should be transported separately as previously noted. Sources are reusable: once collected they can be placed in another home. At the end of the study, all of the sources were returned to the HSPH laboratory for verification of the permeation rate.

4.2.2.3 Field Blanks and Duplicates

In addition to the field samples, the sampling program included about 10% blanks and 10% duplicates. Duplicates were deployed and terminated as described above. They were placed within 3-6 inches of the main CAT. Blanks were transported to the sampling location, activated and immediately closed again. The blank CAT was placed in a resealable plastic bag containing charcoal or carbon paper and left at the sampling location until the exposed CATs were collected.



4.3 Survey Instruments

4.3.1 Questionnaires

Questionnaires are commonly used in indoor air quality studies to characterize potential sources and removal mechanisms within homes (Lebowitz et al., 1989). In exposure assessment, questionnaires can be used to help determine the effects of personal activities on exposure. Lebowitz et al. (1989) identified several key topics which should be addressed in residential air quality questionnaires: (1) physical characteristics—size and age of the home, insulation, primary heating sources; (2) sources and usage—presence and use of supplemental heating sources, cooking stoves, smoking; (3) removal mechanisms—ventilation characteristics and usage, pollutant sinks; (4) occupant activities; and (5) presence and usage of consumer products.

For the Fort McKay study, three questionnaires were developed: the Household Characteristics Questionnaire, the Personal Exposure and Activity Questionnaire, and the Household Activity Questionnaire (see Appendix 4). Questions and formats were drawn from questionnaires used in the TEAM study and the Alberta Oil Sands Community Exposure and Health Effects Assessment Program (Alberta Health, 2000a). All three questionnaires were designed to be completed by the field investigator while interviewing the occupant of the home. Where possible, questions were formatted to allow a yes/no response.

The Household Characteristics Questionnaire was completed during the first visit to the home. It contains questions on six topics: (1) Household and Participant Identification; (2) Household Habitants – sex, age, occupation, and smoking status of household residents; (3) Type of House – type and age of home, physical characteristic of home and yard; (4) Heating, Ventilation, and Air Conditioning Systems; (5) Attached Structures – garages, sheds, porches, greenhouses, etc.; and (6) Household Sources of VOCs – presence and usage of appliances; carpeting; smoking.



The Personal Exposure and Activity Questionnaire was completed after the 24-hour personal and indoor samples were collected. It includes questions on activities during the previous 24-hour period that may be linked to exposure to VOCs. These activities include active and passive smoking, cooking, driving or riding in a motor vehicle, occupational exposures, and the use of appliances and consumer products.

The final questionnaire, Household Activity Questionnaire, was completed after the 96-hour indoor and outdoor samples were collected. This questionnaire identified activities inside the home during the sampling period that may influence VOC concentrations. This includes smoking, appliance use, cleaning, renovation/repair work, hobbies, and crafts. The storage and usage of products containing VOCs, such as gasoline, paints, solvents, adhesives, and cleaning agents was also addressed.

4.3.2 Time-Activity Diary

In addition to the questionnaires, participants in the personal sampling program were asked to complete a 24-hour time-activity diary (Appendix 4). The Time-Activity Log was left with the participants to complete during the sampling period, and a follow-up interview was conducted when the sampler was retrieved 24-hours later. The validity of time-use estimates of both recall and leave-behind diaries were investigated by Juster (1985).

The Time-Activity Log includes spaces to record activity start and end times, and a description of the activity. Examples of activities were not provided. To simplify identification of microenvironments, participants were asked to indicate whether each activity took place indoors (at home, work, school, or other) or outdoors (in a vehicle or otherwise). Robinson (1988) suggested that exposure assessment studies should focus on collecting information on the location of activities.

Data from the questionnaires and time-activity logs were not analyzed for this report, but were used to help identify and explain anomalies in the data.



4.4 Field Procedures

During each sampling season, a study team visited each home three times. Times for each visit were scheduled prior to the first visit, and confirmed by phone a few days beforehand. Just prior to each scheduled visit, participants were contacted by phone to confirm that they would be at home.

During these visits, samplers were deployed and retrieved, and questionnaires completed. Each study team consisted of two or three people. One investigator conducted interviews and completed the questionnaires with the residents, while the remaining investigators set up or retrieved the sampling equipment. Sampling for sulfur dioxide and particulate matter was conducted simultaneously to the VOC sampling. Only those procedures related to the VOC sampling are presented here. Field procedures for each of the three visits are described below. Copies of the field data log sheets are included in Appendix 5.

4.4.1 Visit 1

Upon arrival, indoor and outdoor sampling locations were selected following the sampling location guidelines. During the fall sampling season, locations for three PMCH sources were also selected. Consent was obtained from the resident to place equipment in these locations.

While the sampling equipment was being set up, one team member interviewed the participant and completed the Household Characteristics Questionnaire. The team member also answered any questions that the participant may have had.

The indoor sampling stand was assembled at the indoor sampling location, and the 24-hour and 96-hour indoor samplers were deployed as per the protocol. Replicates and blanks were also deployed at this time. A minimum-maximum thermometer was reset and hung from the sampling stand. PMCH sources were deployed at the selected locations. A sketch of the home's floor plan was prepared, and the location of all



sampling equipment noted.

After the questionnaire was completed, the 24-hour personal sampler was deployed. A copy of the guidelines and a time-activity log were left with the participant. The guidelines for wearing the sampler, and instructions for completing the time-activity log were reviewed with the participant.

Before leaving the home, the participant was reminded of the second and third visits. The outdoor sampling stand was assembled at the selected location, and the 96-hour outdoor sampler deployed along with any replicates or blanks. The outdoor sampling location was noted on the floor plan sketch.

4.4.2 Visit 2

The second visit was scheduled for 24 hours after Visit 1. During the fall sampling season, locations for placement of two CATs were selected, and the CATs deployed. One CAT was usually placed on the indoor sampling stand. The 24-hour indoor and personal samples were terminated and retrieved along with any replicates. The high and low temperatures were recorded, and the thermometer collected. Exposed samplers were transported to the field office to await shipping to the analytical laboratory.

While the sampling equipment was being retrieved, one team member interviewed the participant and completed the Personal Exposure and Activity Ouestionnaire, and the Time-Activity Log.

4.4.3 Visit 3

The third and final visit was scheduled for four days (96 hours) after the first visit. Upon arrival, the participant was interviewed and the Household Activity Questionnaire was completed. The 96-hour indoor samplers were terminated and retrieved, as were the CATs (if applicable). The indoor sampling stand was disassembled, and the equipment removed from the home. Subsequently, the PMCH sources (if applicable) were collected



and stored separately from the CATs.

The 96-hour outdoor samplers were terminated and retrieved, and the outdoor stand disassembled. Exposed samplers, and all other sampling equipment were returned to the field office.



Chapter 5: Sample Analysis

5.1 Target Compounds

The number of VOCs identified in indoor and ambient air reaches well into the hundreds, or perhaps thousands (Shah and Singh, 1988; Miller and Miller, 1998).

Analyzing air samples for all of these compounds would be very costly, and largely pointless. Many of these compounds are found infrequently, and in very low concentrations. Additionally, some compounds are of greater interest due to concerns about health effects resulting from exposure.

Twelve VOCs were selected for study in Fort McKay. Target compounds were selected to mirror those chosen for the Alberta Oil Sands Community Exposure and Health Effects Assessment Program study in Fort McMurray (Alberta Health, 1997). Prior to the Fort McMurray study, a small number of samplers were deployed at oil sands sites, inside and outside of one home in Fort McMurray, and on one person employed in the oil sands industry. The results of the analysis of these samples were used to identify typical VOCs found in indoor, outdoor, and personal air.

In addition to these screening results, several other criteria were used to select the target compounds: (1) toxicity; (2) potential for exposure; (3) availability of a biomarker; and (4) associations with industrial and domestic sources (Alberta Health, 1997). The availability of a measurable biomarker was important for the Fort McMurray study, as biological samples were taken as well as the air samples. No biological samples were taken for the Fort McKay study. The selected compounds and rationale for inclusion are listed in Table 5-1.

5.2 Analysis Procedures

Subsequent to exposure, samples were shipped to the analytical laboratory for analysis. The collected VOCs were desorbed from the carbon pad through solvent extraction. The resulting extract was analyzed through gas chromatography/mass



Table 5-1 Target compounds and rationale for inclusion (Alberta Health, 1997)

Selected Compound	Rationale
benzene	a. toxicity: aplastic anemia, leukemia b. sources: tobacco smoke, automobiles, occupation
toluene	a. toxicity: CNS effects, building related illness (BRI) b. sources: domestic products, solvents
ethylbenzene	a. toxicity: CNS effects, BRI b. sources: alkylbenzines linked to petroleum distillates
xylene (m, p, o)	a. toxicity: CNS effects, respiratory tract irritation b. sources: cleaning agents, paint thinner
n-hexane	a. toxicity: respiratory irritation, BRIb. sources: domestic and industrial solvents
n-heptane n-octane n-nonane n-decane methyl ethyl ketone 3-methylhexane	These compounds were selected based on the results of perliminary sampling on-site at the oil sands. Exposure measures in Fort McMurray / Fort McKay are intended to serve as a possible marker of oil sands emissions.
limonene	Preliminary sampling indicated that this compound was found in relatively high concentrations indoors.

spectrometry (GC/MS) for the target compounds. Analysis procedures and services were provided by Dr. Siu Chan of the Centre for Toxicology in Calgary, Alberta.

5.2.1 Shipping

Exposed samplers were stored at the Fort McKay field office until ready for shipping. Once per week, the collected samplers were packed into cardboard boxes and sent via courier to the laboratory at the Centre for Toxicology in Calgary, Alberta. At least two field blanks were included with every shipment. Each shipment was accompanied by a Chain of Custody/Analytical Request form (see Appendix 5) containing the sample ID numbers and corresponding sampling durations for every sampler. The total number of boxes and samples submitted was also included on the form.



Upon receipt of the samples at the laboratory, the sample ID numbers were removed and a laboratory ID number is assigned to each sample. This was done to ensure that the laboratory staff performing the analysis do not know, and were not biased by the sampling duration. Samples were refrigerated until ready for analysis.

5.2.2 Solvent Extraction

5.2.2.1 Extraction Procedures

The collected VOCs were desorbed from the charcoal pad through solvent extraction. The extraction solvent used was carbon disulfide (CS₂) spiked with internal standards of 2.5 µg/mL benzene-d6, toluene-d8, and ethylbenzene-d10. Sample extraction procedures are given in Table 5-2.

Table 5-2 Solvent extraction procedures

- 1. Remove the exposed sampler from the refrigerator, and bring them to room temperature.
- 2. Place labels from the badge's container onto two autosampler vials.
- 3. Remove the sampler from the can. Ensure that the closure cap is secure, and that the ports are closed.
- 4. Add 1.5mL of extraction solvent through the center port of the badge. Close the lid and agitate gently.
- 5. Let the badge stand for 30 minutes with occasional agitation.
- 6. Transfer about 100 μ L of the extract to one vial and the rest to the other vial for storage. Crimp the caps tightly.

5.2.2.2 Desorption Efficiencies

Solvent extraction may not desorb all of the VOCs collected on the sorbent pad. Desorption efficiencies for all of the target compounds except 3-methylhexane and limonene are published by the manufacturer and range from 0.91 to 1.09 (3M, 1999). However, 3M notes that these are just guidelines, and laboratories should determine desorption efficiencies experimentally.



Desorption efficiencies for each target compound were determined by spiking badges with known amounts of each chemical. Spikes were prepared as per the procedures described by the manufacturer (3M, 1999). The sampler was then analyzed in the same manner as any other sampler. The amount of material recovered was then compared to the amount spiked. All of the experimentally determined desorption efficiencies were very near unity, and a recovery coefficient of 1.0 was used in all calculations.

5.2.3 Gas Chromatography/Mass Spectrometry

After extraction, the sample extract was analyzed through gas chromatography with mass spectrometry detection operating in selected ion monitoring mode.

5.2.3.1 Quality Assurance/Quality Control

For each compound, two controls were prepared from stock solutions and run in every batch of samplers analyzed. The concentration of the controls were 1 μ g/mL for all compounds except m, p-xylene and 2-butanone which were 2 μ g/mL. One control was run after the calibrators, and the other at the end of the analytical sequence. A mild calibrator was run in the middle of the sequence. If the control results deviated more than 20% from the expected range, the analysis was repeated.

5.2.3.2 Analytical Procedures

The sample extracts were analyzed using a Hewlett-Packard 6890/5973 GC/MS operating in selected ion monitoring (SIM) mode. Technical specifications of the instrument are given in Table 5-3. Prior to sample analysis, five calibration standards (0, 0.1, 0.5, 1, and 2 µg/mL) were prepared for each compound and analyzed. Based on these standards, calibration curves were developed for use in quantifying the amount of a compound in the sample extract. Instrumental analysis procedures are given in Table 5-4.



Table 5-3 Analytical instrument specifications

Instrument: Hewlett-Packard 6890/5973 GC/MS

Column: HP 19091V-402 capillary 25.0 m x 200 mm (i.d.) x 1.12 mm (film

thickness).

Carrier gas: Helium

Table 5-4 Instrumental analysis procedures

1. Dispense some of the extraction solvent to the reagent blank vials.

- 2. Inject the reagent blank and samples, calibrators and controls into HP 6890/5973 GC/MS.
- 3. Runs are performed in the following order:
 - a. Reagent Blank
 - b. Calibrator 1 µg/mL (for setting retention times and ion ratios)
 - c. Calibrator 0, 0.1, 0.5, 1, and 2 μ g/mL
 - d. Reagent Blank
 - e. Control 1
 - f. Sample(s)
 - g. Mid-Calibrator: 1 µg/mL
 - h. Sample(s)
 - i. Control 2
- 4. Check the slopes of the calibration curves to ensure that they are acceptable prior to running the samples.

5.3 Calculations

The GC/MS analysis yields a concentration of the selected compound in the extract. The analyte mass per badge was calculated by multiplying the concentration by the volume of extraction solvent used (1.5 mL). The blank-corrected time-weighted average concentration, C (μ g/m³), was calculated using the following equation:

$$C = \frac{M - m}{R \times 1} \times 10^3$$
, (Eqn. 5-1)

where M is the mass of compound on the badge (ng); m is the average mass of compound on the blank badges (ng); R is the sampling rate (mL/min); and t is the sampling duration



(min). The equation assumes a recovery coefficient of 1.0, as determined by the laboratory. As per Gagner (1996), no temperature correction factor was applied. Sampling rates published by 3M (1999) were available for all compounds except limonene. In the absence of a published sampling rate for limonene, an experimentally-determined sampling rate was used. Table 5-5 lists the sampling rates used in the calculation of TWA concentrations.

Table 5-5 Sampling rates (after 3M, 1999)

Commonad	Compline Date (ml /min)
Compound	Sampling Rate (mL/min)
Hexane	32.0
2-Butanone	36.3
3-Methylhexane	28.9
Benzene	35.5
Heptane	28.9
Toluene	31.4
Octane	26.6
Ethylbenzene	27.3
m, p, o-Xylenes	27.3
Nonane	24.6
Decane	23.1
d-Limonene	30.0



Chapter 6: Results and Discussion

6.1 Sampling Overview

The fall and winter sampling seasons were carried out following the protocols and procedures described in the previous chapters. The results of both sampling seasons are presented in this chapter.

The fall season extended from September 23 to October 22, 1999. During this period, a total of 160 samplers, including field blanks and replicates, were deployed at 30 homes in Fort McKay. Of these samplers, 159 were retrieved with one outdoor sampler lost in the field. Results from the personal sampling at two homes were excluded from the analysis because the participants indicated that the badges had not been worn.

At each home, the residents answered a series of questionnaires regarding household characteristics and activities. In addition, air exchange rates were also measured using a passive sampler and tracer system.

The winter sampling season lasted from January 19 to February 4, 2000. Including field blanks and replicates, 164 samplers were deployed of which 162 were retrieved. One indoor and one outdoor sampler were lost in the field. Residents of one of the participant homes declined to participate in the second round of personal sampling, although indoor and outdoor sampling was still undertaken. Of the remaining 29 homes, personal sampling results from three homes were excluded from analysis as the participants indicated that they had not worn the badge.

As in the fall sampling season, the residents of each household completed a similar set of questionnaires. No air exchange measurements were made during the winter sampling period.

Exposed samplers were collected and stored in their sealed containers at the field office. Once per week, exposed samplers were sent to the Centre for Toxicology in Calgary for analysis. Samplers were analyzed promptly, and results returned within six



weeks of the end of sampling.

In addition to the samplers placed in the field, a number of additional monitors were deployed for the purposes of quality assurance and quality control. These included trip blanks to assess method detection limits, and duplicate and triplicate samples to assess precision of the method.

Sampling conditions may affect the performance of the diffusive samplers, and the VOC concentrations at the sampling location. Meteorological conditions such as temperature, wind speed, and wind direction were tracked throughout the duration of the study. Temperatures were also recorded indoors. Air exchange rates were measured to help ensure that adequate face velocities were present at the sampling locations.

6.2 Analysis of Field Blanks

Throughout the course of the study, 27 field blank samplers were deployed and collected. All of these badges were analyzed at the Centre for Toxicology in Calgary. The results from three of the badges were discarded for unusually high toluene levels. Mean analyte masses and standard deviations were calculated based on the remaining 24 field blanks. Raw analysis results for all blank badges are included in Appendix 6.

6.2.1 Background Contamination

In order to accurately quantify the concentration of a compound found at a sampling location, the level of background contamination of the sampling badge must be considered. Each badge may contain some amount of a compound prior to exposure to air, and further contamination may occur during storage and handling of the samplers. By analyzing the amount of each target compound present on the blank badges, the level of background contamination can be assessed.

Based on the analysis of the 24 blank badges, levels of background contamination greater than the detection limit of the analytical instruments were found for six of the



thirteen target VOCs. Table 6-1 gives the mean analyte masses found on the blank badges and the corresponding time-weighted concentrations in air. All results in the study were blank-corrected by subtracting the mean background concentration from the analytical result.

Table 6-1 Mean background masses and concentrations

Substance	Analyte mass (ng/badge)	24-hour TWA (μg/m³)	96-hour TWA (μg/m³)
Hexane	409	8.9	2.2
2-Butanone	18	0.3	0.1
Benzene	23	0.4	0.1
Toluene	674	14.9	3.7
m,p-Xylenes	34	0.9	0.2
Limonene	21	0.5	0.1

6.2.2 Detection Limits

Detection limits for each compound take into consideration the sensitivity of the analytical instruments and the background contamination of each badge. The instrumental detection limit (IDL) is based on a signal-to-noise ratio of three. The signal corresponding to the mass of compound on a badge must be three times greater than the background noise of the analytical instrument in order to distinguish it positively from such noise. The mass of each compound corresponding to this ratio was provided by the analytical laboratory. These masses and the corresponding time-weighted concentrations in air are given in Table 6-2.

In determining the method detection limit, the background contamination of the sampling badges must also be considered. In order to confirm the presence of a compound at the sampling location, the level of analyte found on the badge must be shown to be greater than the amount likely to appear due to background contamination.



This was accomplished by analyzing a number of blank badges. The detection limit was calculated by multiplying the standard deviation of the blank samples by the appropriate value of Students' t to yield a 99% confidence interval. The upper bound of this interval represents the level above which only 1% of blank samples should occur.

Table 6-2 Instrumental detection limits

Compound	Analyte mass (ng/badge)	24-hour TWA (μg/m3)	96-hour TWA (μg/m3)
Hexane	45	1.0	0.2
2-Butanone	90	1.7	0.4
3-Methylhexane	45	1.1	0.3
Benzene	45	0.9	0.2
Heptane	45	1.1	0.3
Toluene	45	1.0	0.2
Octane	45	1.2	0.3
Ethylbenzene	45	1.1	0.3
m, p-Xylenes	90	2.3	0.6
Nonane	45	1.3	0.3
o-Xylene	45	1.1	0.3
Decane	45	1.4	0.3
d-Limonene	45	1.0	0.3

The Students' t-value corresponding to $\alpha=1\%$ (one-tailed) and 23 degrees of freedom (n-1) is 2.500. This factor was multiplied by the standard deviation from the analysis of the blank badges. For seven of the thirteen compounds, the level of background contamination was found to be less than the detection limit of the analytical instruments. Table 6-3 gives standard deviations, and detection limits expressed as masses and converted to time-weighted average concentrations for the remaining six compounds.



For the purposes of this analysis, the method detection limit for those compounds with background badge contamination levels less than the instrumental detection limit was taken as the instrumental detection limit. For the remaining six compounds, the method detection limits was based on the background contamination of the badges. Table 6-4 summarizes the corresponding 24-hour and 96-hour detection limits for each compound.

The detection limits for a number of compounds, most notably hexane and toluene, were relatively high due to background contamination of the sampling badges. Correspondence with the analytical laboratory indicated that these levels were not unusual and were within the manufacturer's specifications.

6.3 Precision

Throughout the study, duplicate and triplicate measurements were taken approximately every ten samples. The analysis of replicate measurements was used to estimate the precision of the sampling method. During the fall sampling season, eight sets of triplicate samplers and four pairs of duplicate samplers were deployed. During the winter sampling season, a total of six triplicate sets and twelve duplicate pairs were deployed. The replicate measurements were spread approximately evenly among the four sampling conditions (24-hour personal and indoor samples; 96-hour indoor and outdoor samples). For reasons of participant convenience, only duplicate personal samples were taken: no triplicates were employed.

6.3.1 Intraclass Correlation Coefficients

Lee et al. (1995) suggested an intraclass correlation coefficient as an appropriate measure of the precision of a passive sampler. This coefficient provides a relative comparison of the variation within duplicate pairs with the variation among sets of duplicate pairs (Koch, 1983). If the variation within duplicate pairs is large relative to the variation



Table 6-3 Background standard deviations and levels of detection

	Standard		MDL (µg/r	
Compound	Deviation (ng/badge)	MDL (ng/badge)	24-hour TWA	96-hour TWA
Hexane	239	597	13.0	3.2
2-Butanone	62	155	3.0	0.7
Benzene	84	210	4.1	1.0
Toluene	261	652	14.4	3.6
m,p-Xylenes	67	169	4.3	1.1
Limonene	58	145	3.3	0.8

MDL - method detection limit

TWA - time-weighted average concentration

Table 6-4 Method detection limits for target compounds

	MDL (μg/m³)			
Compound	24-hour TWA	96-hour TWA		
Hexane	13.0	3.2		
2-Butanone	3.0	0.7		
3-Methylhexane	1.1	0.3		
Benzene	4.1	1.0		
Heptane	1.1	0.3		
Toluene	14.4	3.6		
Octane	1.2	0.3		
Ethylbenzene	1.1	0.3		
m, p-Xylenes	4.3	1.1		
Nonane	1.3	0.3		
o-Xylene	1.1	0.3		
Decane	1.4	0.3		
d-Limonene	3.3	0.8		

MDL - method detection limit

TWA - time-weighted average concentration



between duplicate pairs, the value of the coefficient approaches –1. When the precision of the sampler is high, the variation within duplicate pairs is relatively small and the coefficient approaches a value of +1. Table 6-5 gives the intraclass correlation coefficients for the fall and winter sampling seasons, and the total number of replicates.

Table 6-5 Fall and winter intraclass correlation coefficients

	Intraclass correlation coefficient			
Compound	Fall (n=12)	Winter (n=18)		
Hexane	0.8251	0.5027		
2-Butanone	0.7509	0.9956		
3-Methylhexane	0.9727	0.8261		
Benzene	0.9545	0.8521		
Heptane	0.9867	0.9342		
Toluene	0.8721	0.5061		
Octane	0.9962	0.9877		
Ethylbenzene	0.9104	0.9388		
m,p-Xylenes	0.5959	0.8859		
Nonane	0.9997	0.9998		
o-Xylene	0.9992	0.9515		
Decane	0.9976	0.9998		
Limonene	0.9995	0.9787		

As can be seen in the above table, most of the intraclass correlation coefficients are greater than 0.9, indicating good precision. Six compounds have coefficients less than 0.9 for the fall and/or winter sampling seasons. Of note, five of these compounds (hexane, 2-butanone, benzene, toluene, and m,p-xylenes) are among the six compounds where detectable levels of background contamination were found on the badges. The variation in background contamination explains some loss of precision for these compounds. The equations used in calculating intraclass correlation coefficients and other statistical parameters are included in Appendix 7. It should be noted that the intraclass



correlation coefficients can be greatly affected by the presence of a small number of bad duplicates. For example, the fall intraclass correlation coefficient for m,p-Xylenes increases from 0.596 to 0.920 when one set of replicates is removed.

6.3.2 Relative Standard Deviation

Another commonly-used measure of precision is the percent relative standard deviation (%RSD). Percent relative standard deviation is a ratio of the standard deviation to the mean of a replicate set expressed as a percentage. Table 6-6 gives the median %RSD for the thirteen target compounds. Only duplicate pairs with both measurements above the detection limit were considered. Separate analyses for fall and winter were not performed. Unlike the intraclass correlation coefficient, the median %RSD is relatively insensitive to the presence of bad replicates.

Table 6-6 Median relative standard deviation

Compound	n	Median relative standard deviation
Hexane	23	49%
2-Butanone	6	8%
3-Methylhexane	21	12%
Benzene	26	13%
Heptane	24	5%
Toluene	29	30%
Octane	19	5%
Ethylbenzene	16	7%
m,p-Xylenes	26	6%
Nonane	13	5%
o-Xylene	15	4%
Decane	8	6%
Limonene	22	4%



As with the intraclass correlation coefficients, the compounds with the highest degree of background contamination show the least precision as evidenced by the high RSD values for hexane and toluene. The remaining RSD values were all below 15%, with the majority being less than 10%.

6.4 Sampling Conditions

The performance of a passive sampler such as the OVM 3500 can be affected by the sampling conditions. Factors such as temperature, relative humidity, and face velocity can potentially bias the results. Meteorological conditions such as wind speed and direction can affect outdoor concentrations.

6. 4.1 Outdoor Conditions

The Wood Buffalo Environmental Association operates an air quality monitoring station just north of the Fort McKay Water Treatment Plant. In addition to monitoring a variety of airborne pollutants, the station also monitors meteorological conditions in the area. Continuous measurements of temperature, wind speed, and wind direction are recorded year-round. Precipitation is only measured during the summer, and relative humidity and atmospheric pressure are not measured.

Daily average, minimum, and maximum temperatures for the fall and winter sampling periods are shown in Figures 6-1 and 6-2 respectively. These plots show that the outdoor temperature varied widely throughout the two sampling periods. This is especially true of the winter sampling period where the difference between the minimum and maximum temperatures was 46°C. Gagner (1996) tested the OVM 3500 at temperatures down to -30°C. During the winter sampling period, the temperature fell below -30°C on only two days, and the daily average temperature was below -30°C only on the first day of sampling. Outdoor temperatures and wind speeds for the fall and winter sampling periods are summarized in Table 6-7.



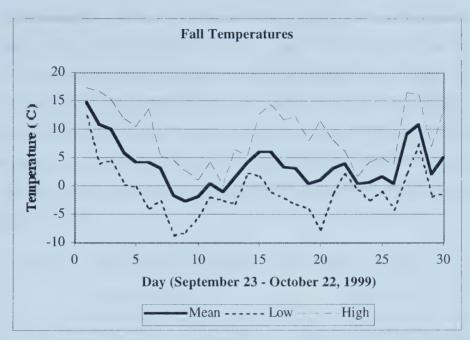


Figure 6-1 Daily mean, high, and low temperatures, fall sampling period

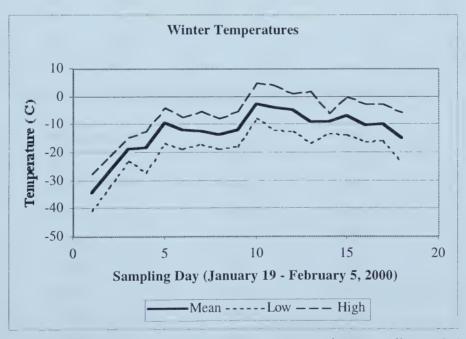


Figure 6-2 Daily mean, high, and low temperatures, winter sampling period

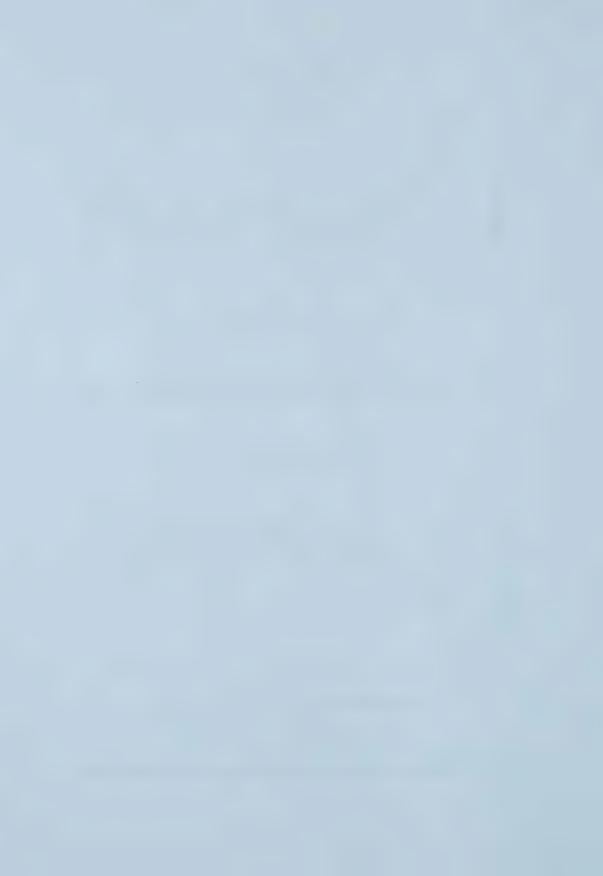


Table 6-8 gives wind speed frequencies for the fall and winter sampling seasons. Wind direction frequencies are plotted in Figures 6-3 and 6-4. The OVM 3500 has been found to perform well at face velocities down to 0.01 m/sec (0.036 km/h) (Tang et al., 1993; Hori and Tanaka, 1996). The minimum wind speed recorded over both sampling periods was 0.2 km/h which should provide adequate face velocity. The wind direction frequencies show that the wind came predominantly from the south, especially during the winter sampling period. During the fall, the wind also frequently came from the north or northwest.

Table 6-7 Average daily fall and winter meteorological conditions

	Temperature (°C)				Wind Speed		
Season	Average	Minimum	Maximum	Average	Minimum	Maximum	
Fall	3.6	-8.7	17.2	8.9	0.5	32.3	
Winter	-12.7	-40.9	5.1	6.8	0.2	20.1	

Table 6-8 Wind speed frequency, fall and winter sampling season

Windspeed (km/h)	Fall	Winter
0-2	3.6%	17.1%
2-5	22.9%	16.9%
5-10	38.9%	44.2%
10-15	20.7%	18.8%
15-20	9.5%	2.8%
20-25	3.5%	0.2%
25-30	0.7%	0.0%
30-35	0.1%	0.0%



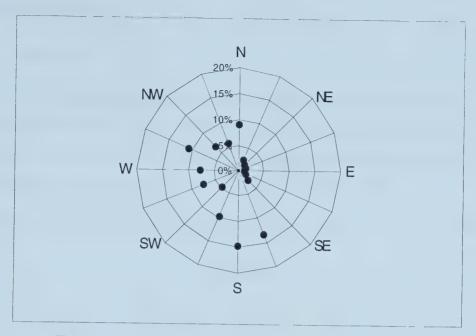


Figure 6-3 Wind direction frequencies, fall sampling season

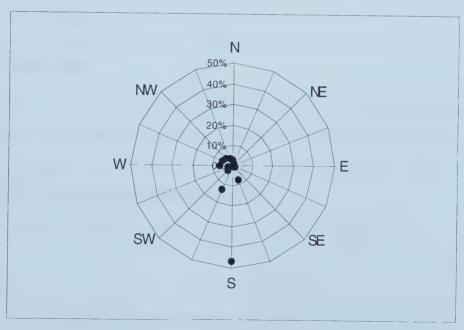


Figure 6-4 Wind direction frequencies, winter sampling season



6.4.2 Indoor Conditions

6.4.2.1 Temperature

Indoor temperatures were measured using minimum-maximum thermometers. Average temperatures were calculated as the mean of the minimum and maximum temperatures. Temperatures for the fall and winter are summarized in Table 6-9. Indoor temperatures were within the sampler's operating parameters (3M, 1999).

Table 6-9 Average, minimum, and maximum fall and winter indoor temperatures

	Temperature (°C)			
Season	Average	Minimum	Maximum	
Fall	20	9	28	
Winter	23	9	30	

6.4.2.2 Air Exchange

Measurements of air exchange were taken only during the fall sampling season. Tracer sources and samplers were deployed inside 28 homes. Samplers inside of two homes went missing during the course of the study. The air exchange rates for the remaining 26 homes are summarized in Table 6-10.

Table 6-10 Summary of air exchange rates, fall sampling season

		Air exchan	ge rate (acn)	
N	Mean	Median	Minimum	Maximum
26	0.39	0.30	<0.01	1.83



The air exchange rates in Fort McKay are similar to those seen in similar studies. Pandian et al. (1998) reported statistics from a database compiled from results of various air exchange studies. Based on measurements from 585 homes in the northwestern United States, the mean and median air exchange rates were reported as 0.41 ach and 0.33 ach respectively. A study of 60 homes in the Northwest Territories found a range of air exchange rates from 0.042 ach to 2.2 ach (Appin Associates, 1991). Of the 60 homes, 35 were found to have air exchange rates of less than 0.3 ach.

6.5 Percent Measurable

The proportion of observations above the method detection limit (MDL) for each compound is summarized in Table 6-11 and 6-12. From the tables, it can be seen that there were a considerable number of observations below the MDL. In general, it appears that most compounds were found more frequently indoors than outdoors. During the fall sampling season, only one compound was detected in more than half of the outdoor samples. Most compounds were detected more frequently in the winter than the fall for all sample types.

Treatment of below detection limit environmental data is a much-discussed topic (Rhodes, 1981; Gillom et al., 1984; Gilbert, 1987; Porter et al., 1988; Helsel, 1990; Lambert et al., 1991; Cressie, 1994; Keith, 1994). Many methods and techniques have been suggested to deal with below detection limit data (Kushner, 1976; Gillom and Helsel, 1986; Cohen and Ryan, 1989; Newman et al., 1989; Travis and Land, 1990). Although below detection limit measurements have traditionally been censored (i. e., reported as "ND" or "<MDL"), many authors contend that these values are valuable and should be reported as originally determined (Rhodes, 1981; Gillom et al., 1984; Gilbert, 1987; Porter et al., 1988; Helsel, 1990; Cressie, 1994).

The proportion of observations below the detection limit was used as a screening tool to determine the type and level of statistical analysis performed. The US EPA (1998)



Table 6-11 Proportion of fall measurements above the detection limit

	96-hour Samples		24-hour	Samples
	Outdoor	Indoor	Indoor	Personal
n	29	30	30	28
Hexane	0%	33%	17%	21%
2-Butanone	0%	57%	43%	46%
3-Methylhexane	28%	63%	33%	50%
Benzene	21%	93%	67%	86%
Heptane	31%	40%	30%	57%
Toluene	24%	97%	57%	75%
Octane	24%	73%	30%	32%
Ethylbenzene	10%	80%	27%	50%
m,p-Xylenes	76%	100%	83%	100%
Nonane	3%	50%	10%	21%
o-Xylene	10%	80%	23%	39%
Decane	0%	20%	10%	11%
Limonene	0%	100%	100%	100%

Table 6-12 Proportion of winter measurements above the detection limit

	96-hour Samples		24-hour	Samples
	Outdoor	Indoor	Indoor	Personal
n	29	29	30	26
Hexane	21%	69%	17%	23%
2-Butanone	0%	21%	17%	19%
3-Methylhexane	100%	100%	53%	69%
Benzene	100%	100%	80%	85%
Heptane	100%	97%	83%	96%
Toluene	48%	100%	57%	62%
Octane	97%	100%	53%	69%
Ethylbenzene	76%	97%	47%	58%
m,p-Xylenes	100%	100%	90%	92%
Nonane	79%	93%	27%	42%
o-Xylene	72%	93%	63%	77%
Decane	0%	59%	10%	19%
Limonene	14%	100%	93%	100%



suggest guidelines to determine the type of analysis appropriate for data sets with varying percentages of below-detection limit observations. For data sets with less than 15% non-detects, substitutional methods (replacing non-detects with half the detection limit or some other number) are appropriate. More complex methods, such as Cohen's maximum likelihood estimators, can be used with data sets with 15-50% non-detects. If a data set has between 50% and 90% non-detects, analysis should be limited to tests of proportions. If only 10% of observations are greater than the detection limit, the data are likely insufficient for further analysis.

For the purposes of this study, only data sets with greater than 50% of observations greater than the MDL were used in detailed statistical analyses and hypothesis testing. Where appropriate, statistical analyses was performed with uncensored data –i.e., the original measurements as reported by the analytical laboratory.

6.6 Distributions

Histograms and normal probability plots for each compound, sample type, and season were prepared (see Appendix 8). Most of the histograms display the characteristic right-skewed appearance of a lognormal distribution. The lognormal distribution has often been applied to describe pollutant concentrations in ambient and indoor air (Mage, 1981; Ott, 1995b).

All distributions with greater than 50% of observations greater than the MDL were tested for lognormality using the Shapiro-Wilk test (see Appendix 7) (Shapiro and Wilk, 1965; Royston, 1993, 1995). A majority of the distributions were found to be lognormal at a significance level of 0.01. The calculated Shapiro-Wilk W statistic and associated probabilities are tabulated in Appendix 8.

6.7 Descriptive Statistics

Given the right-skewed nature of the distributions, the median is a better measure of central tendency than the arithmetic mean. The median is insensitive to extreme data at



both ends of the scale. As long as more than half of the observations are greater than the detection limit, below-detection limit data will not affect the median.

Given the lognormality of many of the distributions, the geometric mean and standard deviation were calculated. For samples with censored data, Cohen's method was used to estimate the mean and standard deviation of the log-transformed data using the US EPA's DataQUEST software (US EPA, 1997, 1998). The results were backtransformed to determine the geometric mean and standard deviation. Geometric means and standard deviations were only calculated when less than half of the observations were below the method detection limit. In the tables that follow, values below the detection limit are indicated by an asterisk (*).

6.7.1 General

Raw analytical results for all samples are tabulated in Appendix 6. Summary statistics for the fall and winter sampling seasons for each target compound are presented in Tables 6-13 through 6-25. For most compounds, the range of concentrations was quite broad. Lower concentrations occur more frequently than high concentrations, but extremely high concentrations were observed for many compounds. The range of concentrations was often two or three orders of magnitude.

In general, personal air concentrations seem to be slightly higher than indoor air concentrations. Both personal air and indoor air concentrations are generally much higher than those observed outdoors. Most compounds were detected more frequently in indoor and personal air than outdoors. The majority of compounds were detected more frequently, and in higher concentrations, outdoors during the winter sampling season than during the fall sampling season.

6.7.2 Aromatics

Summary statistics for the aromatic compounds are given in Tables 6-13 through 6-17. One of these compounds, the m, p-xylenes, was found at detectable levels in nearly



Table 6-13 Fall and winter summary statistics for benzene

96-hour TWA concentration (μg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.8*	1.5	5.2		
	Indoor	4.1	9.1	26	4.1	2.2
Winter	Outdoor	2.3	3.8	4.6	2.3	1.4
	Indoor	5.3	9.8	13	5.1	1.6

^{*} MDL= $1.0 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			_ , ,						
			90th		Geometric	Geometric			
Season	Location	Median	Percentile	Maximum	mean	s. d.			
Fall	Personal	7.0	14	35	7.7	1.9			
	Indoor	5.3	15	19	5.4	2.0			
Winter	Personal	7.8	18	28	7.5	1.8			
	Indoor	7.0	12	21	6.3	1.7			

Table 6-14 Fall and winter summary statistics for toluene

96-hour TWA concentration ($\mu g/m^3$)

	-		90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.5*	5.3	7.4	-	
	Indoor	11	37	170	13	2.4
Winter	Outdoor	3.6*	10	18		
	Indoor	18	30	80	16	1.9

^{*} MDL= $3.6 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric	
Season	Location	Median	Percentile	Maximum	mean	s. d.	
Fall	Personal	21	. 47	52	21	1.8	
	Indoor	20	44	50	18	2.1	
Winter	Personal	23	56	89	17	2.6	
	Indoor	15	38	84	16	2.0	



Table 6-15 Fall and winter summary statistics for ethylbenzene

96-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.1*	1.1		
	Indoor	1.8	5.3	20	1.4	3.6
Winter	Outdoor	1.3	2.7	4.1	0.9	2.8
	Indoor	2.8	7.1	17	3.1	2.1

^{*} MDL=0.3 mg/m³

24-hour TWA concentration (µg/m³)

					40 /	
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	1.0*	6.5	13		
	Indoor	0.0*	4.7	23		
Winter	Personal	3.3	11.2	24	1.7	5.6
	Indoor	0.8*	9.3	24		

^{*} MDL=1.1 mg/m³

Table 6-16 Fall and winter summary statistics for m, p-xylenes

96-hour TWA concentration (µg/m³)

	-		90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	1.3	2.9	8	1.5	1.9
	Indoor	5.2	20	84	5.7	2.4
Winter	Outdoor	3.9	8	15	3.9	1.8
	Indoor	8.7	26	71	10	2.1

24-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	10	23	51	10	1.9
	Indoor	6.7	14	94	7.5	2.2
Winter	Personal	12	40	91	13	2.4
	Indoor	9.7	35	92	11	2.3



Table 6-17 Fall and winter summary statistics for o-xylene

96-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.1*	1.3		
	Indoor	1.8	7.9	29	1.5	4.0
Winter	Outdoor	1.6	3.4	5.6	1.0	3.5
	Indoor	3.3	9.1	24	3.5	2.7

* MDL= $0.3 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	0.0*	8.6	17		
	Indoor	0.0*	5.2	32		
Winter	Personal	4.9	15	45	4.0	3.5
	Indoor	3.8	14	49	2.2	4.9

* MDL=0.3 μg/m³

Table 6-18 Fall and winter summary statistics for hexane

96-hour TWA concentration ($\mu g/m^3$)

	-		90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	1.8*	2.1*		
	Indoor	1.2*	10	71		
Winter	Outdoor	2.3*	4.1	11		
	Indoor	4.3	16	59	5.0	2.7

* MDL=3.2 μg/m³

24-hour TWA concentration (µg/m³)

				40		
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	5.1*	21	30		
	Indoor	2.3*	19	68		
Winter	Personal	4.0*	21	36		
	Indoor	1.7*	15	32		

* MDL=13 μ g/m³



Table 6-19 Fall and winter summary statistics for heptane

96-hour TWA concentration (μg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	1.9	4.9		
	Indoor	0.0*	10	17		
Winter	Outdoor	3.6	5.0	7.7	3.6	1.3
	Indoor	6.0	11	16	5.6	2.0

^{*} MDL= $0.3 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			(1.6 - 1.7 -				
			90th		Geometric	Geometric	
Season	Location	Median	Percentile	Maximum	mean	s. d.	
Fall	Personal	4.6	14	43	2.1	6.5	
	Indoor	0.0*	7.8	19			
Winter	Personal	7.5	23	35	7.5	2.3	
	Indoor	6.3	14	17	4.8	2.8	

^{*} MDL= $1.1 \mu g/m^3$

Table 6-20 Fall and winter summary statistics for octane

96-hour TWA concentration (μg/m³)

	-	Median	90th Percentile	Maximum	Geometric mean	Geometric s. d.
Fall	Outdoor	0.0*	1.1	2.7		
	Indoor	1.6	9.0	42	1.2	5.7
Winter	Outdoor	2.5	3.3	3.7	2.3	1.6
	Indoor	3.8	14	23	4.3	2.0

^{*} MDL=0.3µg/m³

24-hour TWA concentration (µg/m³)

			2 1 20 00 1 1 1 1 2 0 0 0 0 0 0 0 0 0 0				
			90th		Geometric	Geometric	
Season	Location	Median	Percentile	Maximum	mean	s. d.	
Fall	Personal	0.0*	21	95			
	Indoor	0.0*	8.7	20			
Winter	Personal	4.1	38	79	2.4	6.7	
	Indoor	1.1	13	71	1.6	6.2	

^{*} MDL= $1.2\mu g/m^{3}$



Table 6-21 Fall and winter summary statistics for nonane

96-hour TWA concentration (μg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.0*	0.9		***
	Indoor	0.5	3.7	63		
Winter	Outdoor	1.4	1.8	2.3	1.0	2.3
	Indoor	2.2	6.6	185	2.5	3.6

^{*} MDL= $0.3 \mu g/m^3$

24-hour TWA concentration (µg/m³)

					40 /	
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	0.0*	6.0	15	-	
	Indoor	0.0*	0.4*	4.8		
Winter	Personal	0.0*	7.4	440		
	Indoor	0.0*	6.2	610		

^{*} MDL=1.3 μg/m³

Table 6-22 Fall and winter summary statistics for decane

96-hour TWA concentration (μg/m³)

	_		90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.0*	0.0*		
	Indoor	0.0*	12	120	***	
Winter	Outdoor	0.0*	0.0*	0.0*		
	Indoor	1.1	14	440	0.7	17

^{*} MDL= $0.3 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			2 · 110 11 · 1 · 1 · 1 · 1 · 1 · 1 · 1 ·			
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	0.0*	1.6	29		
	Indoor	0.0*	0.9*	26		
Winter	Personal	0.0*	7.6	930	***	
	Indoor	0.0*	0.4*	1300		

^{*} MDL=1.4 μ g/m³



Table 6-23 Fall and winter summary statistics for 2-butanone

96-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.0*	0.0*		
	Indoor	2.3	7.5	33	1.2	6.2
Winter	Outdoor	0.0*	0.0*	0.0*		
	Indoor	0.0*	12.9	110		

^{*} MDL= $0.7 \mu g/m^3$

24-hour TWA concentration (µg/m³)

					(1.5)	
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	0.7*	8.8	12		
	Indoor	0.5*	9.4	13		
Winter	Personal	0.0*	17	45		
	Indoor	0.0*	11	58		

^{*} MDL= $3.0 \mu g/m^3$

Table 6-24 Fall and winter summary statistics for 3-methylhexane

96-hour TWA concentration ($\mu g/m^3$)

		90th			Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	1.1	2.2		
	Indoor	1.3	7.3	18	0.8	7.4
Winter	Outdoor	1.8	3.6	7.1	1.9	1.6
	Indoor	3.1	7.0	18	3.5	1.8
* 1401 - 0.2/3						

* MDL= $0.3 \mu g/m^3$	24-hour TWA concentration (μg/m³)
	Z i lioui i will concentration (p., in)

			2 . 110 41 1		(1011)	
			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	1.8	15	39	1.4	7.9
	Indoor	0.0*	7.6	21		
Winter	Personal	5.2	19	38	3.2	4.8
	Indoor	2.8	11	13	1.6	4.9

^{*} MDL=1.1 μ g/m³



Table 6-25 Fall and winter summary statistics for limonene 96-hour TWA concentration (μg/m³)

	•		90th		Geometric	Geometric
		Median	Percentile	Maximum	mean	s. d.
Fall	Outdoor	0.0*	0.0*	0.0*		
	Indoor	21	80	270	26	2.6
Winter	Outdoor	0.0*	0.9	3.9		
	Indoor	30	86	140	27	2.6

^{*} MDL= $0.8 \mu g/m^3$

24-hour TWA concentration (µg/m³)

			90th		Geometric	Geometric
Season	Location	Median	Percentile	Maximum	mean	s. d.
Fall	Personal	31	65	200	26	2.3
	Indoor	18	80	210	24	2.7
Winter	Personal	23	73	110	22	2.2
	Indoor	15	50	110	17	2.7

all of the samples. Benzene is ubiquitous in indoor and personal air. The remaining compounds are all found in high frequency in indoor air.

Toluene concentrations were the highest amongst the aromatic compounds in indoor air. Maximum concentrations in indoor and personal air of both toluene and m-,p- xylenes exceeded $80~\mu g/m^3$.

6.7.3 Straight-chain aliphatics

Summary statistics for the alkanes from hexane through decane are given in Tables 6-18 through 6-22. Heptane and octane were found relatively frequently in indoor and personal air. Hexane and nonane were found less frequently, and decane was rarely found at detectable concentrations.

No measurable outdoor concentrations of decane were found. The remaining compounds were found more frequently and in higher concentrations outdoors in the winter than the fall.



While none of the observed median alkane concentrations were particularly high, some extremely high individual concentrations were observed. Most notably, 24-hour TWA concentrations of decane and nonane inside of one home were measured at 1300 $\mu g/m^3$ and 600 $\mu g/m^3$ respectively. It was determined that on the first day of sampling, the occupants had used an oven cleaner in the kitchen adjacent to the sampling location. The concentrations fell during subsequent sampling days as evidenced by the 96-hour TWA concentrations of 440 $\mu g/m^3$ and 180 $\mu g/m^3$. The maximum measured concentrations of all compounds except heptane exceeded 50 $\mu g/m^3$.

6.7.3 Other compounds

Summary statistics for the remaining compounds are given in Tables 6-23 through 6-25. Of the three remaining compounds, only 3-methylhexane appeared with any frequency outdoors. No detectable levels of 2-butanone were found outdoors, and only four of 58 outdoor samples showed detectable concentrations of limonene.

Limonene was ubiquitous in indoor and personal air. Median indoor and personal limonene concentrations were the highest of all compounds. Maximum indoor and personal limonene concentrations exceeded 100 $\mu g/m^3$ in the winter, and 200 $\mu g/m^3$ in the fall. While 2-butanone was seen less frequently indoors, concentrations greater than 50 $\mu g/m^3$ were observed.

6.7.4 Comparison of Results to Other Studies

The results of the Fort McKay study were compared to the results of other studies in Table 6-26 through 6-28.

Personal air concentrations from Fort McKay were compared to personal sampling results from the 1990-92 German Environmental Survey (GerES II) (Hoffmann et al., 2000), and from US EPA TEAM studies in New Jersey, California, and North Dakota (Wallace et al., 1987c; Wallace et al., 1988). Levels of aromatics appear to be



Table 6-26 Comparison of personal air concentrations

	Fort McKay Fall a	Fort McKay Fort McKay Fall ^a Winter ^a	GerES IIb	New Jersey Fall °	New Jersey New Jersey Fall ° Winter	California Spring ^d	N. Dakota Fall
			Personal Ai	Personal Air Concentration (μg/m³)	on (μg/m³)		
Z	28	26	113	344	48	19	24
benzene	7.0	7.8	Ţ	16	22	7.5	
toulene	21.1	23.7	69				
ethylbenzene	< 1.1	3.3	7	7.1	8.9	3.7	2.8
m, p-xylenes	10.2	12.2	16	16	22	11	7.7
o-xylene	< 1.1	4.9	5	5.4	∞	4.4	3.2
hexane	5.1	4.0	6				
heptane	4.6	7.5	5				
octane	< 1.2	4.1	2			2.3	
nonane	< 1.3	< 1.3	3				
decane	< 1.4	< 1.4	5			7	
2-butanone	< 3.0	< 3.0	44				
3-methylhexane	1.8	5.2	4				
limonene	30.5	22.7	32				
8 modion of 24 h	in I can can can a series						

a median of 24-hour personal air samples

^b median of 7-day samples in Germany (Hoffmann et al, 2000)

° average of median 12-hour day and night samples in Bayonne/Elizabeth, New Jersey (Wallace et al, 1987) ^d average of median 12-hour day and night samples in Pittsburg/Anitoch, California (Wallace et al, 1988)

* average of median 12-hour day and night samples in Devil's Lake, North Dakota (Wallace et al, 1987)



Table 6-27 Comparison of indoor air concentrations

	Fort McKay	Fort McKay Fort McKay	Canadian	Dutch	Kanawha	Sherwood	Chemicod
	Fall a	Winter a	Homes b	Homes °	Valley d	Park Fall °	Park Winter *
			Indoor Air	r Concentration	on (µg/m³)		
Z	30	29	757	134	35	32	32
benzene	4.1	5.3	'n	7	2.1		2.9
toulene	11.3	17.8	41	40		14	ì
ethylbenzene	1.8	2.8	∞	8	2.7	2.9	1.4
m, p-xylenes	5.2	8.7	20	12*	7.3	9.5	5.7
o-xylene	1.8	3.3	9		2.6	3,3	2.1
hexane	< 3.2	4.3	1	4			
heptane	< 0.3	0.9		ю			
octane	1.6	3.8		2			
nonane	0.5	2.2		4			
decane	< 0.3	1.1	31	6			
2-butanone	2.3	< 0.7					
3-methylhexane	1.3	3.1		7			
limonene	20.7	30.3	20	26			

^a median of 96-hour indoor air samples

^b mean of 24-hour samples collected across Canada (Otson et al, 1994)

° median of 5-7 day samples in post-war homes in the Ede, the Netherlands (Lebret et al, 1986) ^d median of 3 week samples in the Kanawha Valley, West Virginia (Cohen et al, 1989)

e median of 24-hour samples in Sherwood Park, Alberta (Byrne, 2000)

* all xylenes

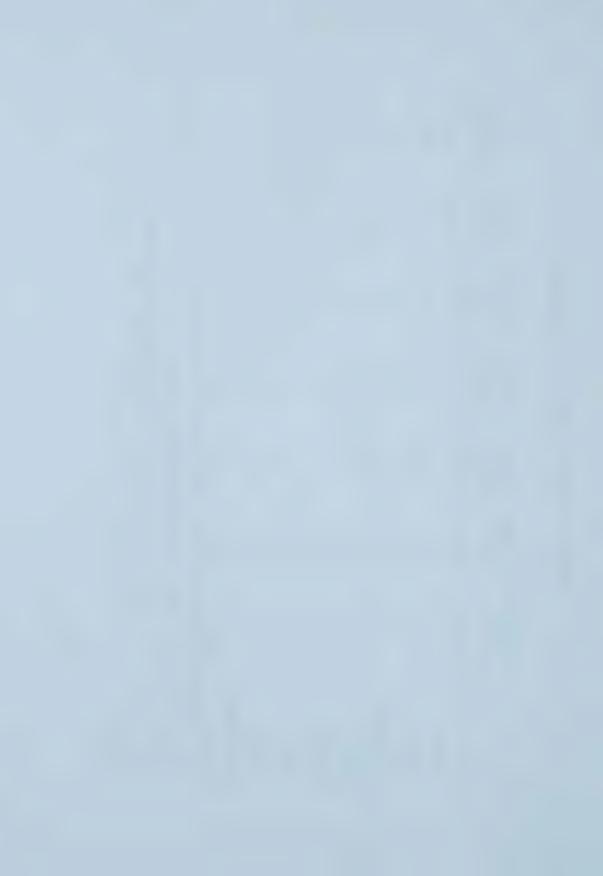


Table 6-28 Comparison of outdoor air concentrations

	Dank May	To-11 Mary	r.		,			
	Folt McKay	Fort McKay Winter	Dutch homes ^b	Kanawha Valley °	NewJersey Fall ^d	California Spring °	Sherwood Park Fall ^f	Sherwood Park Winter ^f
			Oni	tdoor Air Con	Outdoor Air Concentration (µg/m³)	/m³)		
Z	29	29	319	35	98	10	32	32
benzene	< 1.0	2.3	c	2.5	7.2	1.9		1.2
toulene	< 3.6	3.6	\$	· * .			1.3	
ethylbenzene	< 0.3	1.3	0.4	1.1	m	0.0	9.0	0.2
m, p-xylenes	1.3	3.9	3*	2.3	6	2.2	1.8	0.9
o-xylene	< 0.3	1.6		-	m	0.7	0.6	0.5
hexane	< 3.2	< 3.2	7)
heptane	< 0.3	3.6	1					
octane	< 0.3	2.5	<0.3			0.5		
nonane	< 0.3	1.4	<0.3					
decane	< 0.3	< 0.3	9.0			3.8		
2-butanone	< 0.7	< 0.7						
3-methylhexane	< 0.3	1.8	6.0					
limonene	< 0.8	< 0.8	<0.3					
a median of 06-hour outdoor air	mir outdoor oir	committee						

median of 96-hour outdoor air samples

^b median of 5-7 day samples outside of homes in Ede and Rotterdam, the Netherlands (Lebret et al, 1986)

^d average of median 12-hour day and night samples in Bayonne/Elizabeth, New Jersey (Wallace et al, 1987) ° median of 3-week samples outside of homes in the Kanawha Valley, West Virginia (Coehn et al, 1989)

* average of median 12-hour day and night samples in Pittsburg/Antioch, California (Wallace et al, 1988) f median of 24-hour samples in Sherwood Park, Alberta (Byrne, 2000)

* all xylenes



lower in Fort McKay than in the German and New Jersey studies. In particular, toluene levels in the German study were three times those found in Fort McKay, and benzene concentrations in New Jersey were double those found in Fort McKay. The New Jersey study took place in an urban area with significant industrial/chemical manufacturing activity. Aromatic levels in the California and North Dakota TEAM studies were similar to those found in Fort McKay. The California results were from the cities of Pittsburg and Antioch which were selected for their proximity to petroleum refining activity (Hartwell et al., 1987). The North Dakota results are from a rural, agricultural community far from any industrial activity.

As with the personal air concentrations, levels of aromatic compounds in indoor air were lower in Fort McKay than in several other studies. Toluene levels in Canadian and Dutch homes were more than double those found in Fort McKay (Lebret et al., 1986; Otson et al., 1994). The Canadian study also found xylene and decane levels which were noticeably higher than those measured in Fort McKay (Otson et al., 1994). Concentrations reported in the Kanawha Valley (Cohen et al., 1989) and Sherwood Park studies (Byrne, 2000) were comparable to those found in the Fort McKay study.

Outdoor VOC levels in Fort McKay during the fall were lower than those observed in other studies. Winter levels were comparable to those reported for the Dutch study, the Kanawha Valley study, and the California TEAM study. Concentrations in Fort McKay were higher than those found in Sherwood Park in the winter. Both fall and winter levels in Fort McKay were lower than those found in the TEAM study found in urban New Jersey.

6.8 Hypothesis Testing

The hypothesis of the main study states that increases in regional industrial activity do not result in significantly greater levels of VOCs in outdoor, indoor, and personal air in Fort McKay. This hypothesis cannot be tested until measurements are



taken subsequent to the planned industrial development in the region. During this phase of the study, however, three other hypotheses were tested:

- (1) levels of VOCs in indoor air are not significantly greater than those found outdoors;
- (2) levels of VOCs in personal air are not significantly greater than those found indoors;
- (3) levels of VOCs during the winter sampling period are not significantly greater than those found during the fall sampling period.

For all hypothesis testing, replicate samples were averaged and the mean values used in all calculations.

6.8.1 Indoor-Outdoor Relationships

Studies in the United States and Europe have shown that concentrations of VOCs are typically higher in indoor air (de Bortoli et al., 1986; Lebret et al., 1986; Wallace, 1987; Cohen et al., 1989). The Alberta Health study in Fort McMurray found that indoor VOC concentrations were generally higher than those found outdoors (Alberta Health, 2000b, c). Summary statistics for the Fort McKay study appear to support these conclusions. All compounds were found at detectable levels as frequently or more frequently indoors than outdoors (see Tables 6-11 and 6-12). Median concentrations of all compounds were also greater indoors than outdoors (see Tables 6-27 and 6-28).

During the fall sampling period, only one of the thirteen target compounds was detected in more than half of the outdoor samples, compared to nine of thirteen in the 96-hour indoor samples. In the winter, eight compounds were detected in more than half of the outdoor samples, and twelve compounds were found in more than half of the indoor samples. Formal hypothesis testing was performed only on those compounds found in more than 50% of both the outdoor and indoor samples.



6.8.1.1 Wilcoxon Signed Ranks Test

As the data consisted of matched pairs of indoor and outdoor samples, the Wilcoxon signed ranks test was applied to the differences to test the following null hypothesis:

H₀: there is no difference between 96-hour indoor and outdoor VOC concentrations. H₁: 96-hour indoor VOC concentrations are greater than outdoor VOC concentrations.

The test statistics were calculated using Microsoft Excel following the procedures given in Siegel and Castellan (1988). The significance level of the tests was α =0.05. As the direction of the difference is predicted, the test is one-tailed. For the fall and winter hypothesis testing, Table 6-29 gives the number of non-zero differences, N; the calculated Wilcoxon signed ranks test statistic, T+; and the probability, P, that T+ is greater than or equal to the calculated value when H_0 is true.

Table 6-29 Indoor-outdoor Wilcoxon signed ranks tests

		Fal			Wint	ter
	N	T+	P	N	T+	P
3-Methylhexane				29	393	7.4 x 10 ⁻⁵
Benzene				29	429	2.4 x 10 ⁻⁶
Heptane				29	399	4.3 x 10 ⁻⁵
Octane				29	388	1.1 x 10 ⁻⁴
Ethylbenzene				28	385	1.7 x 10 ⁻⁵
m,p-Xylenes	29	435	1.3 x 10 ⁻⁶	29	405	2.5 x 10 ⁻⁵
Nonane				27	352	4.5 x 10 ⁻⁵
o-Xylene				27	350	5.5 x 10 ⁻⁵

For all of the compounds tested, the probabilities are very small and we can reject the null hypothesis at a significance level of α =0.05 (or much lower, for that matter). It is concluded that for the selected compounds, indoor concentrations are significantly



Table 6-30 Fall and winter Indoor/Outdoor ratios

Indoor/Outdoor Ratio

	Fort	McKay	Dutch ^a	TEAM CAb
	Fall	Winter	Winter	Winter
Hexane	4.8	1.9	2	
2-Butanone	5.4			
3-Methylhexane	4.7	1.7	2	
Benzene	5.1	2.3	2	2.0
Heptane		1.7	3	
Toluene	22	5.0	8	
Octane	5.5	1.5	>3	2.1
Ethylbenzene	6.3	2.2	5	2.1
m,p-Xylenes	3.9	2.2	3*	2.2
Nonane	1.4	1.6	>15	2.5
o-Xylene	6.4	2.1		2.2
Decane		3.3	>15	2.7
Limonene	79	116	>80	47

^{*} total xylenes

greater than outdoor concentrations. This is consistent with the findings of previous of studies of indoor VOCs.

6.8.1.2 Indoor/Outdoor Ratios

Ratios of median indoor/median outdoor concentrations were calculated. Where the median indoor or outdoor concentration was less than the instrumental detection limit (IDL), ratios were calculated by substituting the IDL for the median concentration. If both the indoor and outdoor median concentrations were below the IDL, no ratio was calculated. Ratios for both the fall and winter sampling seasons are given in Table 6-30. Ratios from a Dutch study of over 300 homes (Lebret et al., 1986), and from the 1987

a ratio of median indoor/median outdoor concentrations (Lebret et al, 1986)

b ratio of median indoor/median outdoor concentrations (Hartwell et al, 1992)



TEAM study in Southern California (Hartwell et al., 1992) are given in Table 6-30 for comparison.

Indoor/outdoor ratios were greater than one for all compounds. In many cases, the ratios are much greater than one. For most compounds, winter ratios in Fort McKay are comparable to winter ratios found in the Dutch and American studies. Indoor/outdoor ratios of nonane and decane were much higher in the Dutch study. The Fort McKay indoor/outdoor ratio for limonene exceeded 70 in both the fall and winter seasons. This is consistent with values found in the Netherlands and in California.

As only one compound was found in more than half of the fall outdoor samples, the fall ratios must be viewed somewhat cautiously. For most compounds, indoor/outdoor ratios were larger during the fall sampling season.

While the infiltration and accumulation of outdoor VOCs can contribute to indoor VOC levels (Lewis, 1991), the magnitude of the indoor/outdoor ratios suggests the presence of dominant indoor VOC sources. The relationship between indoor and outdoor VOC concentrations clearly indicates that fixed site ambient monitoring does not adequately reflect indoor concentrations, or, by implication, actual human exposures.

6.8.2 Personal-Indoor Relationships

A number of studies have indicated that VOC concentrations in personal air are generally higher than and closely related to concentrations in indoor air (Wallace, 1997; Hartwell et al., 1992; Alberta Health, 2000b, c). This result is not unexpected considering the amount of time individuals typically spend indoors, especially in their own homes (Szalai, 1972; Chapin, 1974; Leech et al., 1996).

While the main TEAM study did not directly measure indoor air, overnight personal air samples were considered as a surrogate (Wallace et al., 1985, 1988). The overnight samples indicated that indoor sources are a significant contributor to personal exposure. The daytime personal air samples showed that factors such as occupation and



personal activities resulted in further elevated levels. The 1987 TEAM study in California found that personal air concentrations were generally greater than those measured by fixed monitoring in kitchens and living rooms (Hartwell et al., 1992). The Alberta Health study in Fort McMurray concluded that personal air levels were slightly higher than and closely related to levels in indoor air (Alberta Health, 2000b, c).

In Fort McKay, the percent detectable and median concentrations found in 24-hour personal air samples were slightly higher than those found in 24-hour indoor air samples. Only those compounds found in greater than 50% of both the personal and indoor air samples were considered in the formal hypothesis testing.

6.8.2.1 Wilcoxon Signed Ranks Test

As with the indoor-outdoor hypothesis, the Wilcoxon signed ranks test was applied to the differences between matched pairs. In this case, the null and alternative hypotheses were formulated as follows:

H₀: there is no difference between 24-hour personal and indoor VOC concentrations.
 H₁: 24-hour personal VOC concentrations are greater than indoor VOC concentrations.

The significance level of the tests was α =0.05. As the direction of the difference is predicted, the test is one-tailed. Table 6-31 gives the number of non-zero differences, N; the calculated Wilcoxon signed ranks test statistic, T+; and the probability, P, that T+ is greater than or equal to the calculated value when H_0 is true.

For the fall sampling season, the null hypothesis can be rejected in the cases of benzene and m, p-xylenes. At the 5% significance level, concentrations of these compounds in personal air were greater than those found in indoor air. For fall toluene and limonene levels, the null hypothesis cannot be rejected and it is concluded that there is no significant difference between concentrations in personal and indoor air.



Table 6-31 Personal-Indoor Wilcoxon signed ranks tests

		Fall			Winte	er
	N	T+	P	N	T+	P
3-Methylhexane				20	183	0.002
Benzene	28	285	0.03	25	264	0.003
Heptane				24	265	0.0005
Toluene	28	222	0.33	25	257	0.006
Octane				18	135	0.016
m,p-Xylenes	28	289	0.03	25	277	0.001
o-Xylene				20	159	0.022
Limonene	28	242	0.19	26	244	0.041

During the winter sampling season, the null hypothesis can be rejected at the 5% significance level for all eight of the compounds tested and it is concluded that all of the compounds were found in significantly higher concentrations in personal air than indoor air. The implication of these results is that personal activities, both inside and outside of the home, can result in elevated local VOC concentrations. Substantial exposures may be occurring outside of the home. These may include occupational exposures, exposure to mainstream or sidestream cigarette smoke, and exposures while driving or pumping gas. The use of consumer products containing VOCs may also result in elevated VOC concentrations in local air with limited influence on areal VOC levels. These results suggest that indoor fixed site monitoring does not fully represent an individual's actual exposure.

6.8.2.2 Spearman Rank-Order Correlation Coefficients

Although personal air concentrations were found to be higher than indoor air concentrations in most cases, it remains likely that the concentrations are closely related. Studies have indicated that people spend upwards of two-thirds of their time inside their own homes (Szalai, 1972; Chapin, 1974; Leech et al., 1996), so VOC concentrations



inside the home should be very influential on total personal exposures. As such, there should be a positive correlation between personal and indoor air concentrations. In this case, the hypotheses are:

 H_0 : there is no association between VOC concentrations in personal and indoor air; H_1 : there is an association between VOC concentrations in personal and indoor air.

Using matched pairs of personal and indoor air VOC concentrations, Spearman rank-order correlation coefficients were calculated using Microsoft Excel and following procedures given by Siegel and Castellan (1988). Table 6-32 gives the number of matched pairs, N; the correlation coefficient, r_s ; and the probability, P, that r_s is greater than or equal to the calculated value when H_0 is true.

Table 6-32 Personal-Indoor Spearman rank-order correlation coefficients

		Fall			Winte	er
	N	r _s	P	N	r _s	P
3-Methylhexane				26	0.708	2.6 x 10 ⁻⁵
Benzene	¹ 28	0.345	0.036	26	0.682	6.2 x 10 ⁻⁵
Heptane				26	0.858	1.1 x 10 ⁻⁸
Toluene	28	0.499	0.0034	26	0.724	1.4 x 10 ⁻⁵
Octane				26	0.883	1.1 x 10 ⁻⁹
m,p-Xylenes	28	0.456	0.0074	26	0.884	1.0 x 10 ⁻⁹
o-Xylene				26	0.640	2.2 x 10 ⁻⁴
Limonene	28	0.699	1.8 x10 ⁻⁵	26	0.769	2.2 x 10 ⁻⁶

The probabilities given in the table indicate that all of the correlations are significant at the α =0.05 level. The null hypothesis can be rejected for all of the compounds tested during both the fall and winter sampling seasons, and it is concluded that there is a significant association between VOC concentrations in personal and indoor air.



The correlation coefficients for the compounds tested during the fall and winter season were all greater than zero indicating positive association. Several compounds had correlation coefficients exceeding 0.8. The correlation coefficients ranged from 0.345 to 0.699 in the fall, and from 0.640 to 0.884 in the winter.

The r_s values indicate that personal and indoor VOC concentrations were more heavily correlated during the winter than the fall. Correlation coefficients were calculated for four compounds during the fall season. All of these compounds were more heavily correlated during the winter. Correlations of three of the compounds – benzene, toluene, and m, p-xylenes – were much greater in the winter. The increased correlation between personal and indoor air in the wintertime is not unexpected. In periods of cold weather, people are likely to spend more time indoors, thereby increasing the influence of indoor air concentrations on personal exposures.

6.8.3 Fall-Winter Relationships

There have been numerous studies looking into seasonal variations in VOC concentrations. Cheng et al. (1997) found that outdoor VOC concentrations in downtown Edmonton, AB were highest in the winter and lowest in the summer. Similar results have been found in California (Hartwell et al., 1992). Additionally, concentrations in personal air were also found to be significantly greater in the winter.

Seifert and Abraham (1989) found that indoor VOC levels were 2-3 times greater between November and April than between May and October. Although Fellin and Otson (1994) found that indoor VOC levels were not well-correlated with outdoor temperatures, mean indoor VOC concentrations were observed to be higher when the temperature was less than 15° C.

In Fort McKay, nearly all of the target compounds were detected more frequently in outdoor, indoor, and personal air during the winter than the fall. Only those compounds which were detected in more than half of the fall and winter samples were considered in



formal hypothesis testing.

6.8.3.1 Wilcoxon Signed Ranks Tests

The Wilcoxon signed ranks test was performed on matched pairs of fall and winter samples. The differences were calculated by subtracting the winter concentration from the corresponding fall concentration. The hypotheses to be tested are given as:

H₀: there is no difference between fall and winter VOC concentrations;

H₁: winter VOC concentrations are greater than fall VOC concentrations.

The significance level for the test was set at α =0.05. As the direction of the difference is predicted, the test is one-tailed. As the difference is predicted to be negative, the T- statistic was used. Results for the 96-hour and 24-hour samples are given in Tables 6-33 and 6-34 respectively. Each table gives the number of non-zero differences, N; the calculated Wilcoxon signed ranks test statistic, T-; and the probability, P, that T- is less than or equal to the calculated value when H_0 is true.

Table 6-33 Fall-Winter Wilcoxon signed ranks test results

	9	6-hour O	utdoor		96-hour l	ndoor
	N	T-	P	N	T-	P
3-Methylhexane				29	-375	0.00033
Benzene				29	-320	0.013
Toluene				29	-289	0.061
Octane				29	-391	8.8 x 10 ⁻⁵
Ethylbenzene				29	-350	0.0021
m,p-Xylenes	28	-363	0.00013	29	-346	0.0027
o-Xylene				28	-311	0.0070
Limonene				29	-259	0.18



Table 6-34 Fall-Winter Wilcoxon signed ranks test results

	24-hour Personal Air			24	24-hour Indoor Air		
	N	T-	P	N	T-	P	
Benzene	24	-162	0.37	30	-260	0.29	
Heptane	23	-207	0.018				
Toluene	24	-153	0.47	30	-162	0.074	
m,p-Xylenes	24	-215	0.032	30	-315	0.045	
Limonene	24	-108	0.12	30	-184	0.16	

Outdoor Air

In the outdoor samples, hypothesis testing was performed for only one compound, m, p-xylenes. From the result, the null hypothesis can be rejected at α =0.05 and it is concluded that winter concentrations of m, p-xylenes were significantly greater than fall concentrations.

Although no formal tests were performed, similar conclusions for other compounds can be drawn based on the frequency of detection. In the fall, only one compound, m, p-xylenes, was found in more than half of the samples. The remaining twelve compounds were found in 31% or less of the outdoor samples including four compounds – hexane, 2-butanone, decane, and limonene – which were not found in detectable levels in any of the outdoor samples. By contrast, five compounds – 3-methylhexane, bezene, heptane, octane, and m, p-xylenes – were found in all or nearly all of the winter outdoor samples. Three other compounds – ethylbenzene, nonane, and o-xylene – were found in greater than 70% of the winter outdoor samples. Of the four compounds not found in the fall outdoor samples, both hexane and limonene were found, albeit relatively infrequently, in the winter outdoor samples.

Increases in outdoor VOC concentrations during the winter have been attributed to a number of potential causes including meteorology and decreased photochemical



reactivity (Hartwell et al., 1992; Cheng et al., 1997). Meteorology is likely an important factor in Fort McKay. In the winter, vertical mixing in the atmosphere is limited. In the Fort McKay region, the winter mixing height is typically 300-500m compared to around 800m in the fall and 1600-2000m in the summer (Bovar, 1996). During the winter sampling season, winds were predominantly from the south. Wind directions were more evenly distributed about the compass during the fall sampling period, although south winds were most frequent. As the major industrial point sources and the majority of highway traffic are south of the community, south winds may result in a greater influence of these sources on ambient VOC concentrations in Fort McKay.

Indoor Air

For the 96-hour indoor samples, the null hypothesis can be rejected at the 5% significance level for all compounds except toluene and limonene. One cannot conclude that indoor levels of toluene and limonene were greater in the winter than the fall. For the remaining six compounds, one can conclude that indoor VOC concentrations were significantly greater in the winter than the fall.

One possible explanation for elevated winter VOC concentrations is a decrease in ventilation during the colder season. Windows and doors are opened and left open less frequently, and air conditioners are seldom used in winter. Combined with the presence of constant VOC sources indoors and the infiltration of higher concentrations of VOCs in outdoor air, lower ventilation rates may lead to the accumulation of greater concentrations of VOCs in the indoor air.

The fact that significantly elevated indoor levels of toluene and limonene were not found in the winter suggests that concentrations of these chemicals are not driven by constant indoor sources and air exchange rates. Both toluene and limonene are found in many common consumer products. Toluene is found in gasoline, nail polish, cosmetics, paints, adhesives, cleaning products, dyes, and inks amongst other products (ATSDR,



1994). It is also a component of cigarette smoke. Limonene is a common flavor and fragrance additive in food, household cleaning products, and perfumes (IPCS, 1998). The use of these products inside of the home is probably similar throughout the year. It should also be noted that toluene and limonene are the compounds found in the highest concentrations inside of the home. The frequent use of consumer products containing toluene or limonene may result in relatively high transient concentrations which dominate other factors, such as ventilation rates, in determining overall indoor concentrations of these compounds.

As with the 96-hour indoor samples, the levels of toluene and limonene measured in 24-hour indoor air samples were not significantly greater in the winter than the fall. Additionally, the null hypothesis cannot be rejected for 24-hour indoor air levels of benzene. Levels of m, p-xylenes were again found to be significantly greater in winter than fall. The discrepancy between 96-hour and 24-hour indoor samples in the results for benzene, likely reflects the influence of activities inside the home. The 24-hour TWA concentrations were more sensitive to transient elevations in VOC concentrations than the 96-hour samples. Averaging the concentrations over a four-day period has the result of smoothing "spikes" caused by short-term activities, such as smoking or consumer product use, inside of the home.

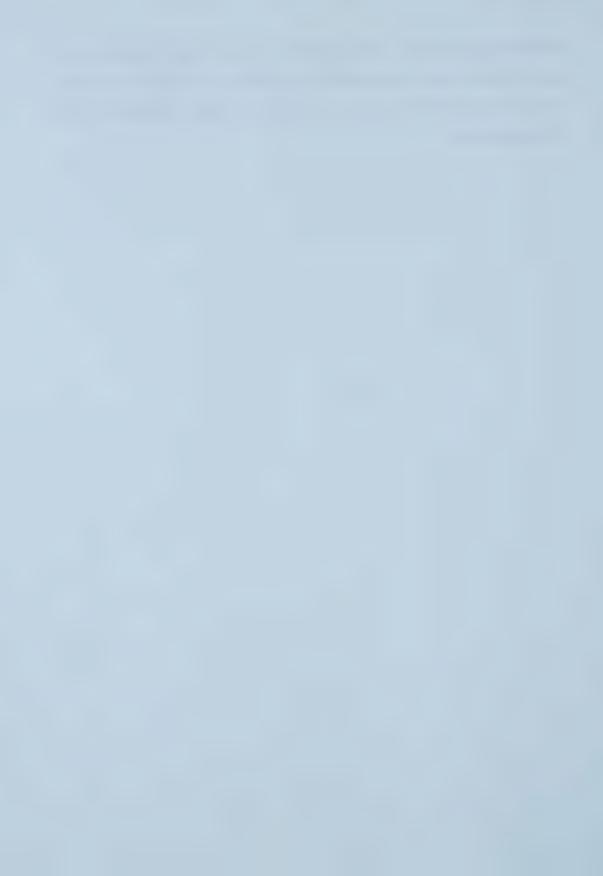
Personal Air

Amongst the five compounds tested in personal air, both heptane and m, p-xylenes were found to be in significantly higher concentrations in the winter than the fall. Given the elevated winter levels in both outdoor and indoor air, this result is not surprising.

Levels of benzene, toluene, and limonene in personal air were not found to be significantly greater during the winter than the fall. Again, this may be attributed to the year-round use of consumer products containing these compounds. The differences



between fall and winter levels of benzene and, in particular, toluene in personal air are smaller than those found between fall and winter indoor concentrations. This points to exposures outside of the home, and the use of products resulting in localized increases in VOC concentrations.



Chapter 7: Discussion and Recommendations

7.1 Discussion

Based on the results of the Fort McKay VOC sampling several trends can be seen about the study hypotheses. First, indoor VOC concentrations were significantly greater than outdoor concentrations. Most compounds were detected more frequently and in higher concentrations in indoor air than in outdoor air. The differences were often quite large: indoor-outdoor ratios for all compounds were greater than one, and many exceeded two or three. Second, VOC concentrations in personal air frequently exceeded indoor concentrations. Although the differences were not great, most were statistically significant, especially in winter. The third trend is that concentrations of many VOCs are significantly greater in outdoor, indoor, and personal air in the winter than in the fall. This may be attributable, in part, to meteorological conditions, and reduced ventilation characteristics during winter.

None of these conclusions were unexpected, and the results seem to confirm the findings of similar studies undertaken elsewhere in Canada, the United States, and Europe. VOC levels in Fort McKay are comparable to those found in the aforementioned studies. In fact, outdoor concentrations in Fort McKay were often lower than those found in more densely urbanized and industrialized areas. Fort McKay is largely free of the influences of heavy motor vehicle traffic, and industrial emissions seem to be diluted rapidly with distance from the source.

The results suggest that indoor VOC sources are more influential on personal exposure than outdoor sources, including major industrial point sources. All of the target VOCs were found more frequently and in significantly greater concentrations indoors than outdoors. While indoor concentrations may be attributed in part to the infiltration and accumulation of VOCs from the outside, the magnitudes of the differences point to the presence of indoor sources. Indoor levels of most VOCs in Fort McKay were similar to or less than levels found in other studies in Canada, the United States, and in Europe.



This suggests the existence of sources, such as building materials and consumer products, common to different geographic areas.

Indoor concentrations for most compounds varied greatly between homes, often spanning a range of 2-3 orders of magnitude. Outdoor concentrations varied much less. This further indicates the dominance of local sources inside of the home. Indoor concentrations also varied over the course of the four-day sampling period. These fluctuations may be attributed to transient activities and product usage, which result in short-term elevations in VOC levels.

Personal air concentrations of most compounds were strongly correlated with indoor air concentrations. This was not surprising, as most people spend a majority of their time inside of their homes. Despite this association, levels of most VOCs in personal air were found to be significantly greater than the corresponding indoor air levels. This result points to the influence of personal activities, both outside and inside the home, on personal exposure. Outside of the home, elevated personal VOC levels may be due to occupational exposures, exposure to mainstream or sidestream tobacco smoke, or activities such as driving and pumping gas. Inside the home, activities such as smoking or consumer product use can lead to very localized elevations in VOC concentration that impact personal exposure without significantly raising indoor air concentrations.

The suggestion that personal activities and indoor sources are the dominant influences on human exposure to VOCs has implications on the management and regulation of VOCs in the environment. Reducing ambient VOC emissions to the atmosphere will likely not affect a proportionate reduction in exposure, and by implication, in the risk to human health posed by exposure to VOCs. That being said, VOCs in the atmosphere are precursors to the production of ground-level ozone and photochemical smog which presents further risks to human health. Environmental decision-making is a complex process where protection of public health is only one of many factors that must be considered.



7.2 Recommendations

While the results seem to indicate that industrial emissions do not strongly influence personal exposure to VOCs, the primary objective of this study was to collect baseline information to directly test this hypothesis. A similar set of measurements should be taken subsequent to the planned industrial expansion in the region, and compared with the baseline results.

In addition to the air samples, a great deal of ancillary information was collected in the form of questionnaires and time-activity data. Analysis of this material in conjunction with the sampling results may yield further insight into the sources, activities and other factors influencing personal exposure to VOCs.

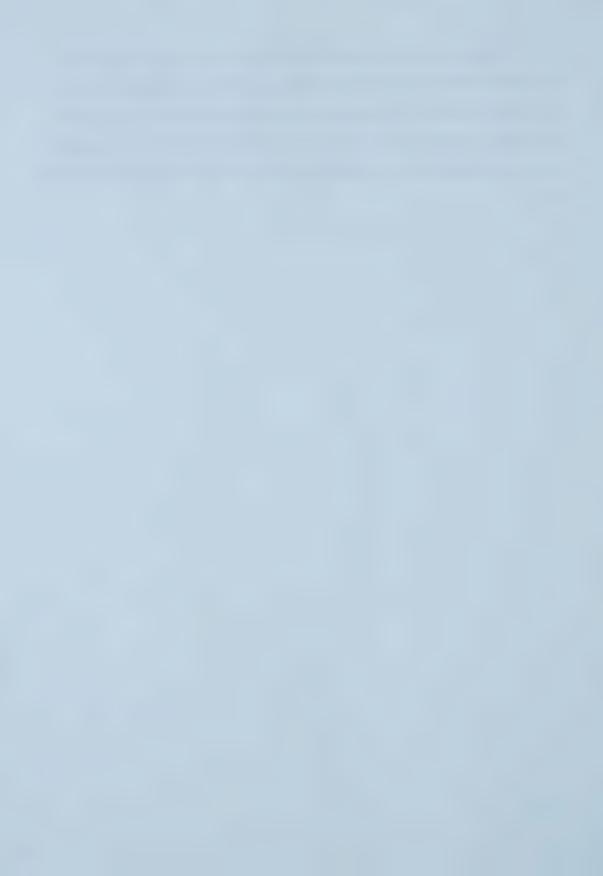
From the experience garnered through the implementation of this study, a number of recommendations can be made to investigators conducting similar studies. The sampling duration should be increased from 4 to 7 days. This would reduce the number of below detection limit samples. Additionally, some authors have suggested that even longer sampling periods are required to accurately estimate long-term exposure distributions (Wallace et al., 1994). Increasing the personal sampling duration would also be useful, although it may make it more difficult to recruit participants. Participants in this study were often wary of wearing the sampler for a 24-hour period.

While the questionnaires were completed satisfactorily, the quality of the timeactivity log was somewhat lacking. Methods to improve the quality of the data should be investigated. This may involve a redesign of the diary form, or refinement of the interview techniques to better coax information from reluctant subjects.

If further studies are carried out in the oil sands region, additional compounds should be targeted. Compounds that are found in the industrial emissions and are without significant indoor sources should be investigated. Many of the compounds selected as markers of oil sands activity did have indoor sources, making it difficult to pinpoint their origin.



It is also important to remember that VOCs are only one class of compounds amongst the multitude of environmental pollutants. Other priority pollutants should be identified and studied. Finally, exposure assessment only represents one link in the human health risk model. If possible, exposures should be linked with sources and health outcomes to provide a complete picture of the health risk posed by environmental pollutants.



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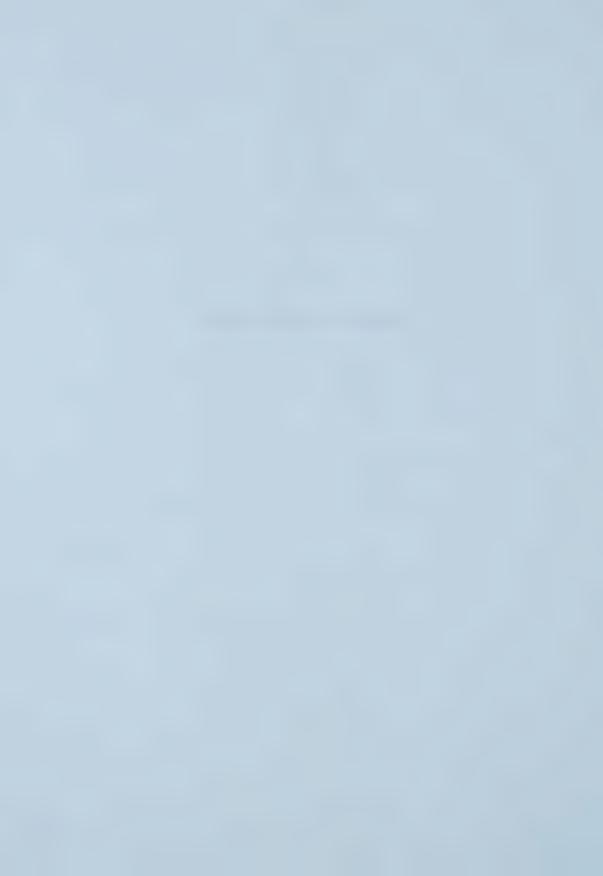
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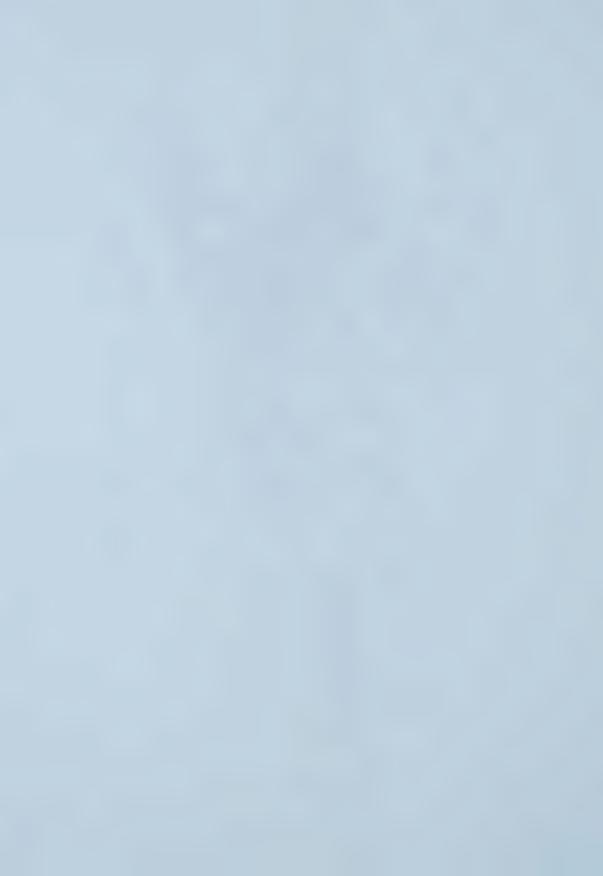
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Appendix 1: Map of Fort McKay







Appendix 2: Recruitment Materials

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FORT MCKAY INDUSTRY RELATIONS CORPORATION

August 10, 1999

Dear Community Members of Fort McKay,

Community members are concerned with Air Quality (air that we breathe) in Fort McKay. We are also concerned about the high rate of various diseases such as asthma, neverending flu, itchy watery eyes and skin, etc. Therefore, an Air Quality and Exposure Monitoring Study is proposed, to find out what McKay people are being exposed to. The Ft. McKay IRC has hired three people from the community to work with a team of experts from the University of Alberta to do the study. The purpose of this study is to help us better understand what is affecting the air that we breathe.

We will interview approximately 40 people using questionnaires, but at least 30 homes are needed to participate in this very important study. Information will be collected and air-sampling devices will be place at each home. Two air samples will be taken at each home (one indoors and one outdoors) for 4 days in September/October and again in February/March 2000. One person from each home will be asked to wear a personal air-sampling device for a 24-hour period, (these personal air-sampling devices are about the size of a badge)

The information in the questionnaires is very important for identifying possible sources of Volatile Organic Compounds (VOC's), Sulphur Dioxide (SO2) and Particulate Matter (PM). The study workers will also fill out a Household and Time Activity Questionnaires at each home. The Household questionnaire contains questions such as; type and size of your home, type of heating, ventilation system being used, types of other chemicals used around home, etc. The Time Activity Questionnaire contains questions such as; in the past 24 hours have you pumped your own gas, used tobacco products, air fresheners, insecticides, cosmetics, etc.

Information collected from each home and person will be kept confidential. This study is NOT intended to pry into personal lives. We are ONLY trying to find out what we are being exposed to. Therefore, we are asking for your cooperation in order to get successful results from this study.

As well, the study workers will be able to answer any questions you may have regarding the questionnaires. If you have any questions, please contact Madeline Delisle at 828 - 4417 or 799 - 2538. The study will begin August 16/99 and it will end around April 2000.

Thank you for your cooperation,

Madeline Delisle, Socio-Economic Coordinator



General Delivery, Fort McKay, Alberta TOP-1C0





Study Overview

The study will be looking at three types of air pollution: volatile organic compounds, sulphur dioxide and inhalable particulate matter.

Households will be selected at random from a list of eligible households, and participants recruited via a door-to-door campaign. The study in general, and the role and responsibilities of the participants will be explained at this time. If the participant agrees to participate in the study, a suitable sampling date and time will be scheduled. The study team will distribute an appointment reminder card.

After being recruited the participant will be visited by the study team on three occasions.

Visit 1

The study team will arrive at the scheduled time on the scheduled date. The sampling devices will be employed inside and outside the house to measure the levels of pollutants. The indoor samplers will be placed in the main living area of the home. Both indoor and outdoor samplers will be placed approximately 1.5 m off the ground. There will be three types of samplers used. Two of the samplers are small and silent badge-type samplers (5-10 cm across). These samplers will be left in place for 4 days. The third sampler is approximately 7" in diameter and 20" high. It will be left in place for only 1 day.

One adult from the household will be selected to wear one of the small badge samplers for a 24-hour period. This will measure the level of pollution in the air being breathed by the individual. The sampler clips onto the collar of a shirt or coat. It should be worn at all times during the sampling period, but can be removed and placed nearby when sleeping or bathing.

The indoor and personal samplers will be placed first to minimize the burden on the householders.

Visit 2 (24 hours later)

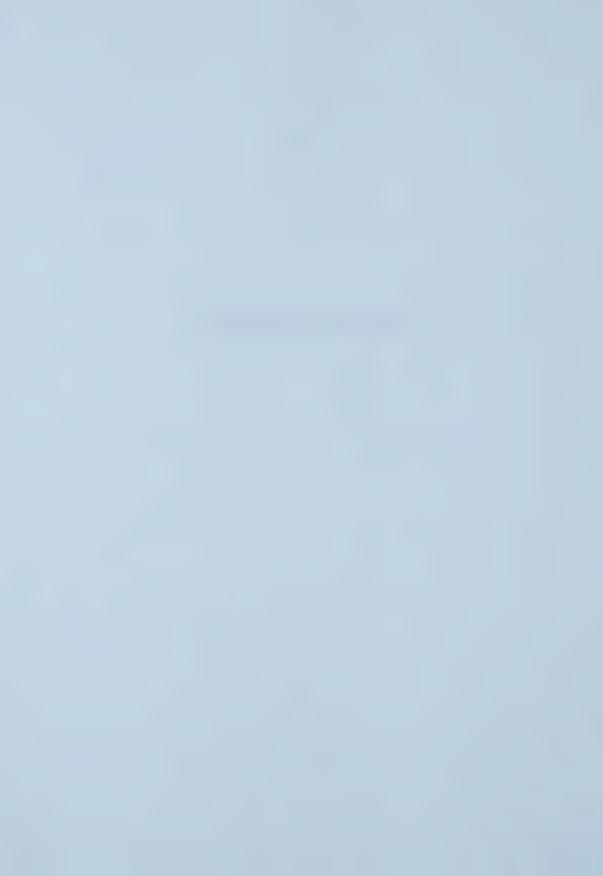
After 24 hours, the study team will return to the home. The large indoor and outdoor samplers will be collected. The sampler being worn by the household member will also be collected at this time. This individual will be asked to complete a 24-hour activity diary. This will help to identfy any activities or locations which may have contributed to exposure to pollutants.

Visit 3 (4 days later)

The remaining indoor and outdoor samplers will be collected. A Household Characteristics Questionnaire will be completed via a brief interview. This will help identify additional factors which may impact the levels of pollutants inside the home.



Appendix 3: Air Exchange Protocol



AIR EXCHANGE MEASUREMENT

1. Scope

This document is intended to provide the necessary details for the determination of indoor/outdoor air exchange rates in relatively small enclosures such as homes, apartments, or small offices. Following the procedure below, air exchanges rates can be quantified over the range 0.10 to 2.5 air changes per hour (ACH). The limit of detection is about 3.0 ACH.

2. Introduction

The measurement of air exchange rate (AER) is accomplished using a tracer gas under steady-state conditions, and a passive sampling technique followed by sample analysis with a gas chromatograph and electron capture detector (GC/ECD).

This method is based upon the technique developed by Dietz et al(1). An inert, non-toxic, tracer chemical, perfluorinated methylcyclohexane (PMCH), is allowed to permeate into the enclosure for 24 hours. During this period a steady-state concentration is theoretically established based upon partly the permeation rate of the PMCH source, the volume and temperature of the enclosure and its average air exchange rate. Now, the passive sampling device, a capillary adsorption tube (CAT), is located in the enclosure and allowed to collect PMCH for a fixed period of time ranging from 12 hours to one week. The PMCH permeation source remains in the enclosure for the duration of the sampling period. The passive sampling device is returned to the laboratory for determination of the amount of PMCH collected. Given the above variables, the collection rate of the CAT, and conversion factors, the average air exchange rate can be calculated. The PMCH source is removed one day after CAT sampling is complete, then it is returned to the lab for post-experimental permeation rate verification.



3. PMCH sources

PMCH sources have a nominal permeation rate of 375 ng/min. at 24-25 degrees C. and a useful lifetime of about 4-5 years. The permeation rate in proportional approximately to temperature, 3% per degree C. For a batch of sources prepared with the same materials at the same time the permeation rate has an associated relative standard deviation (RSD) less than 3%.

A. Preparation

Apparatus, Materials, Supplies

22 mm aluminum bullet shells and holder PMCH (Aldrich Chemical) 50 ml to 100 ml graduated glass beaker autopipette for transferring 0.4 ml silicone rubber solid tubing aluminum plug-cutting tool silicon high vacuum grease crimper 7 mm punch razor blades, single edge electromechanical vibrating engraver or equivalent lab tissue paper disposable rubber gloves #3 cork borer polyurethane foam labels 0.5cmx2.5cm clear tape 3/4"

Procedure

- 1. Engrave an ID on each bullet shell. The ID should be HSPH yy-nnn where yy are the last tow digits of the year made and nnn is the next sequential number.
- 2. Using the punch and hammer, carefully expand the open end of each shell only slightly to facilitate later insertion of the silicone plug. Place the engraved shells sequentially in the shell holder.
- 3. Lay a piece of silicone rubber solid tubing in the aluminum plug jig and carefully cut fixed length plugs with a razor blade. Cut one plug for each source.
- 4. Using gloves, apply a very thin layer of silicone grease to the circumferential surface of the plugs being careful not to get grease on the flat surfaces.
- 5. Calculate the total ml of PMCH needed: number of PMCH sources multiplied by 0.4 ml per source.
- 6. Transfer the calculated amount of PMCH plus a small additional amount to the graduated glass beaker.
- 7. With the autopipette, transfer 0.4 ml PMCH to 6 shells.
- 8. Carefully insert/press a rubber plug into each shell until it is just flush with the top edge.
- 9. Crimp the plugged end of each shell with the special crimper tool.
- 10. Remove excess grease if any with a piece of tissue and replace the shell in the holder.
- 11. With a hack saw cut the polyurethane foam into blocks of 2cm(L) x 3cm(W) x 5cm(H).
- 12. Bore two holes: one, straight through the 3cm dimension at 4cm(H); the second hole to be also about 3cm long, but from the center of the just bored hole through the 5cm dimension, but not straight through.
- 13. Insert a source through the first 3cm hole into the second 3cm hole of the polyurethane plug so that the end of the source with the silicone rubber plug just barely protrudes into the first 3cm hole of the polyurethane plug.



- 14. Prepare a small label (0.5cmx2.5cm) with the ID of the PMCH source and attach it securely to the polyurethane plug with a piece of clear tape all the way around.
- 15. Repeat the process until all sources are made. Place them in a box and store beneath another vented hood away from any potential contact of PMCH with CATs.

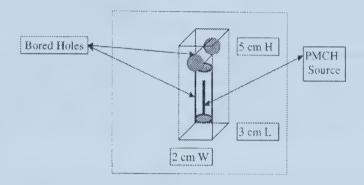


Figure 1. Polyurethane Holder and PMCH Source

B. Determination of permeation rate.

Apparatus, Materials, Supplies

PMCH permeation sources Analytical balance with a readability/accuracy/precision of 0.1 mg. Plastic tweezers Worksheet template

Procedure

- 1. The PMCH source must be at least 3 weeks old prior to any weighing.
- 2. On the template, record the date, time, and temperature. Record the IDs of the PMCH sources.
- 3. Make sure the balance pan is clean (gently wipe with a fine artist brush) and rezero the balance.
- 4. Using the plastic tweezers, carefully extract the PMCH source from its polyurethane block holder and place on the balance pan.
- 5. Allow the reading to stabilize and record the weight. A new source weighs between 1.8 and 2.0 gm. Whereas one at the end of its useful life is usually at or below 1.2 gm.
- 6. Remove the source from the balance pan and replace it in the polyurethane holder.
- 7. Check the zero and reset if necessary.
- 8. Weigh 9 more sources, then reweigh one of the previous nine by random selection.
- 9. Continue this procedure until all PMCH sources have been weighed and recorded.
- 10. If the weighing session is the first time the sources have been weighed, the stop here.
- 11. If this is the second or a subsequent weighing, then the permeation rate may be calculated. For a newer source at least 3 weighing sessions about 2 weeks apart each, are necessary for confirmation of a constant permeation rate. Sources should be weighed twice each, before and after field deployment.
- 12. The permeation rate is calculated by taking the difference in two weights from different weighing sessions, multiplying by 10^{-9} to convert grams to nanograms, and dividing by the time interval in minutes.



$$R_{p} = [(W_{Tf} - W_{Tf}) * 10^{-9} (ng/gm)] / [(Tf - Ti) x K]$$
 (1)

where

 $R_n = Permeation Rate in ng/ml$

 W_{Tf} = final weight of permeation source in gm.

 $W_{Ti} = initial$ weight of permeation source in gm

Tf = date and time of final weighing

Ti = date and time of initial weighing

K = factor for converting days to minutes (1440 minutes/day) and/or hours (60 minutes/hour)

13. General example/discussion: a total of 4 weighing sessions, 2 before and 2 after. Assuming the temperature to be 24 degrees C. for the interval between the first two sessions and the last 2 sessions, the permeation rate should reflect the same equilibrium conditions and be the same within experimental error. The permeation rate between the 2nd and 3rd weighing sessions represents the time interval during field deployment. Providing the temperature remained at 24 degrees C. and there was no mishandling of sources, the permeation rate should be the same as that measured in the lab. (Sources returned from the field should be weighed as soon as possible.) Any change in the permeation rate should obviously be consistent with filed temperatures.

Permeation rate for the field at other than 24 degrees C. should also be calculated by applying the appropriate temperature correction factor to the lab measured rate, i.e. the rate obtained from the 1st/2nd and/or 3rd/4th session. The corrected rate should be close to the rate calculated for the 2nd/3rd session rate. When using the permeation rate for the AER calculation, select the rate which is most consistent with actual source history. For this one may consider that to reach a new permeation equilibrium at a different temperature, takes only a day or two compared to the 3 week duration needed for newly prepared sources. For home where there is a diurnal variation in temperature, make the correction based on the average temperature determined by max-min thermometers.



4. Cleaning of CATs

The CAT sampling device consists of a short length of glass tubing (6.35 cm L x 0.6cm OD x 0.4cm ID) containing a small amount of a carbonized adsorbing material which is sandwiched in the middle by stainless steel screens. An identification number (ID) is permanently engraved on each sampler. The ends of the CAT are capped with either a polyurethane cap of a polyethylene cap. CATs are cleaned by thermally desorbing any adsorbed compounds from them at an elevated temperature in an inert nitrogen atmosphere.

Apparatus, Materials, Supplies:

23 position cleaning rack with attached nichrome heating coils variable voltage transformer low voltage, high current transformer automatic programmable shut off timer (1500 watt) ultrahighpurity nitrogen gas (tank with pressure regulator and needle valve) standard lab tubing (rubber of polyethylene) to connect the gas tank/valves to the rack flowmeter, 500 ml/min carbon paper and/or activated charcoal tea bags cleaning worksheet template resealable plastic bag

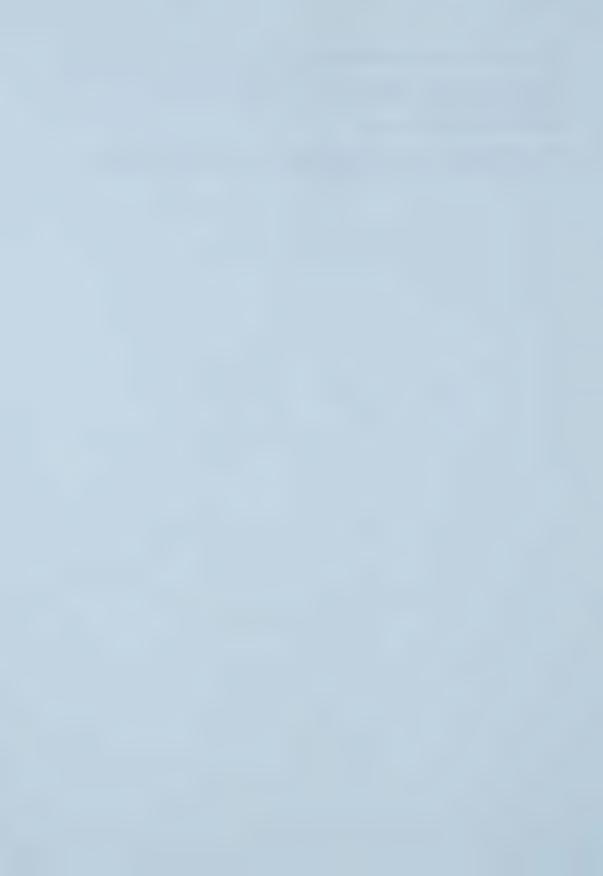
Procedure:

- 1. On the worksheet, enter your name, date of cleaning, and IDs of CATs. Note any unusual CATs.
- 2. Remove the protective caps from 23 CATs and insert the CATs through the coils into the rack's retaining silicone O-rings. The rack is on the upper shelf of the cabinet below the fume hood. Make it protrude a few inches by sliding it toward the operator.
- 3. Turn on the nitrogen gas tank valve, adjust the pressure regulator to about 10 psi.
- 4. Attach a flowmeter to any of the 23 CATs and adjust the needle valve for a flow of about 15 ml/min.
- 5. Check the flow in the remaining 22 CATs to be in the range of 10-100 ml/min.
- 6. Remove the flowmeter.
- 7. With the variable voltage transformer set to zero, turn on the timer:
 - A. Press the T1
 - B. Press the min button until 25 has registered.
 - C. Press the Outlet 1 to activate the outlet, red light on.
- D. Slowly turn the variable voltage transformer dial to a reading of 80. This should produce a just barely visible red-orange glow in the heating coils.
 - E. Press Start on the timer.
- 8. After 25 minutes have elapsed, the timer automatically shuts off voltage to the variable voltage transformer. Allow about 15 more minutes for the heating coils to cool.
- 9. Replace the protective caps on 22 of the 23 CATs.
- 10. Turn off the nitrogen gas tank main valve, pressure regulator, and needle valve.
- 11. Remove the 23rd CAT with no cap and recap at both ends.
- 12. Remove the 22nd CAT and recap the one open end.
- 13. Proceed in similar fashion until all the CATs have been removed and recapped. Minimize the time spent doing this to reduce the amount of air that can diffuse into the CAT.



- 14. Place all the CATs in a plastic resealable bag containing protective carbon paper of 2 activated charcoal tea bags.
- 15. Label the bag: number of CATs, date cleaned, and initials. Store in a labelled drawer.
- 16. Place the worksheet in the Clean/QC file.
- 17. Allow the rack to cool down.
- 18. Replace the rack in its original position.

Safety: Perform this work in the fume hood area with no combustible solvents nearby. Attach a sign in a convenient location to indicate the high temperature hazard.



5. Quality Assurance

Apparatus, Materials, Supplies:

23 cleaned CATs

special gas chromatograph with autosampler and integrator (described below) silicone grease disposable latex gloves (non-powdered)

For most projects, all CATs are analyzed before being sent out to the field. For projects with many CATs (>500) each bag of 23 CATs is at least subsampled to check for contamination. The size of the subsample may vary but may never be less than 3 CATs (10%).

Upon QA analysis, CATs must have < 1.0 pl PMCH, or a peak at tr ~ 1.3 minutes with an area count $< \sim 50000$ counts. The actual area count must be determined by first establishing the value for 1.0 pl. This is easily done by determining the area count for a lab blank (=0.0 pl) and a standard PMCH in the range of 2.0 pl. If the CAT has < 5 pl PMCH (as measured from a recent standard curve) then it can be rerun. If the rerun is < 1.0 pl PMCH, then the CAT may be accepted, otherwise it must be recleaned by the usual process. All data and information must be recorded on the cleaning worksheet and the CAT QA worksheet.

Follow the same procedure for CAT analysis (described below).



Preparation of Standard CATs (for analysis)

Purpose and Design

A series of CATs are prepared with known amounts of PMCH (and optionally PDCH). Each analytical run of samples is accompanied by a full set of CAT standards covering the range of interest of PMCH. The standards are used to construct calibration curves for calculating the amount of PMCH in unknown samples.

A PMCH generator is used. It consists of a source of inert nitrogen gas flowing over a temperature-controlled PMCH source. Flow is measured by a soap-bubble flowmeter and temperature controlled by a constant temperature water bath. Aliquots of PMCH vapor in nitrogen are removed sequentially with a series of gas-tight syringes of increasing volumes through a T-septum arrangement downstream of the generator.

Apparatus, Materials, Supplies

Ultrahigh purity nitrogen gas tank with regulator, $20~\mu m$ id glass capillary and holder, and connecting tubing. Cleaned and QA'd CATs

Temperature controlled water bath and copper tubing

20 ml midget impinger

Chrononmeter of stopwatch

50 ml burette class A

glass T

tubing soap bubble solution

gas-tight syringes: 10, 25, 50, 100, 250, and 500 µl.

charcoal paper of charcoal tea bags

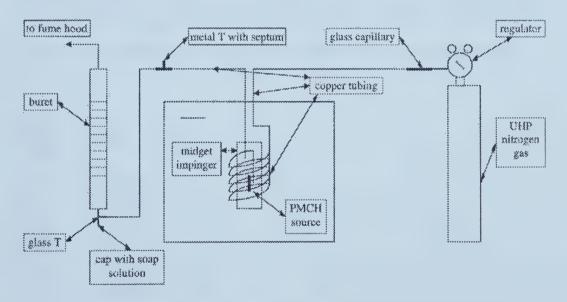


Figure 2. PMCH generator



Figure 2. PMCH generator

Procedure:

1. Determine the nitrogen flowrate

Increase the regulator adjustment so that the secondary pressure is about 20 psi which corresponds to a flow of about 30 ml/min. Squeeze the bulb at the bottom of the glass tee to set in motion a soap bubble in the buret. When the bubble intersects the 50 ml line, start the chronometer; when the bubble intersects the 40 ml line, stop the chronometer. Record the elapsed time in seconds. Repeat two more times. Using the average of the 3 time readings calculate the nitrogen flow rate:

$$F (ml/min) = (10 ml \times 60 sec/min) / average time (sec)$$
(2)

- 2. Reweigh the standard PMCH source in the midget impinger at least once per month and use equation (1) to calculate the standard PMCH source permeation weight, rp-std and record all data and information on the standard CAT worksheet.
- 3. Calculate the concentration of PMCH in the generator:

PMCH (pl/
$$\mu$$
l) = [r_{b-std} (ng/min) x (24.45 nl/350 ng) x 1000 pl/nl] / [F (ml/min) x 1000 μ l/ml] (3)

where (350 ng/24.45 nl) is a molecular weight-molecular volume conversion factor. When $r_{p-md} = 375$ and F = 30, then PMCH (pl/µl) = 0.87 pl/µl.

- 4. Assemble from 1 to 9 sets of cleaned and QA'd CATs. Each set has 9 CATs. Every CAT must have an orange-brown silicone septum on the numbered end and on the plain end a black polyurethane cap of a red polyethylene Caplug, no. #EC-4. Record the CAT IDs on the Standard CATs worksheet.
- 5. Add the indicated µl of PMCH from the generator to the designated CATs using the syringe shown below.

syringe
10 μl syringe
10 μ1 syringe
10 μl syringe
25 μl syringe
50 μl syringe
100 μl syringe
250 µl syringe
500 μl syringe
500 μl syringe

A. Check each syringe-needle for blockage by withdrawing the needle to about 80% of syringe volume, placing the needle tip in a beaker of water, and depressing the plunger. Look for air bubbles and remove the needle from the water while still depressing the plunger. Wipe the tip with lab tissue. If



there is blockage, determine whether it's in the needle or the polytetrafluoroethylene (PTFE) needle retainer. Clean the former with the supplied wire. Clean the latter with the plunger. Be very careful not to deform, damage, or lose any parts. Use a low-power stereomicroscope if necessary.

- B. For each of the "0" CATs pierce the CAT septum with the clean empty 10 μl syringe-needle, remove the needle and return the CAT to its storage position.
- C. Repeat B, but with the clean empty 500 µl syringe-needle.
- D. For the "2" to "20" CATs, insert the appropriate size syringe/needle into the metal T-septum on the PMCH generator and slowly "pump" the plunger at least 3 times. Set the plunger so that the PTFE tip end intersects the appropriate volumetric marking on the syringe. Withdraw the syringe from the generator septum.
- E. Insert the syringe needle through the correspondingly appropriate standard CAT septum until the needle is within 5mm of the SS screen, and slowly depress the plunger all the way.
- F. Remove the syringe needle and replace the CAT in its designated location.
- G. Repeat D. through F. until all "2" to "20" standard CATs have been prepared.
- H. For the "40" to "200" CATs, follow the same procedure as above except first withdraw air from the CAT before introducing the PMCH. This prevents pressure buildup and septum loosening. The amount of air to withdraw is twice the amount of standard PMCH to be introduced. E.g. withdraw 80 μ l when preparing the 40 μ l standard CAT.
- I. Place some charcoal paper of charcoal tea bags in the standard CAT box, close, and store for a least 4 hours before using.
- J. Make sure that all information has been recorded and store the worksheet in the file.

GC-ECD analysis of CATs

Introduction

The amount of PMCH adsorbed on CATs is determined by GC-ECD analysis. A very complete discussion of the GC (Varian Model 6000) and the technique can be found in Dietz, R. et al. This discussion is strictly limited to the operation of the system at HSPH.

Apparatus, Materials, Supplies

Varian GC with ECD; GC heavily modified in semi-multi-dimensional configuration for analysis of PMCH.

Hewlett-Packard 3393A integrator

5% H, and 95% N, carrier gas

Strip chart recorders: 0-1 mv, 0-2 mv, 0-5 mv, and 0-10 mv.

Custom in-house built 23 sample-position autosampler

Chrontrol Lab Timer-Electrical Controller for 1 or 2 circuits.

Silicone grease

Q-tips

Lab supplies/expendables, e.g. tissues gloves, etc.

Analysis worksheets from templates.

Carrier gas is 5% H_2 and 95% N_2 . House supplied air is regulated to 30 psi and provides the air pressure necessary for operation of the 4 6-port switching valves integrally located on the GC, and for maintaining a tight seal on the autosampler's 24-port switching valve (op cit).



A Hewlett-Packard 3393A integrator is attached to the integrator signal lead of the GC. The integrator parameters and Basic language have been used to automate data acquisition and preliminary data reduction. Further signal acquisition is obtained on a strip chart using the GC recorder signal. Also the temperature of the special external Porapak GC column (op. cit.) is monitored by a thermocouple with the signal (0-2 mv)displayed on a strip chart recorder.

See the indicated Appendix below for the settings of all the instrumentation.

Appendix A. Parameters for GC.

Appendix B. Parameters for Integrator operational settings.

Appendix C. Program of Integrator data reduction.

Appendix D. Program for Timer which controls the recorder pens.

Appendix E. Recorders' settings.
Appendix F. Autosampler setting

Procedure: Autosampler

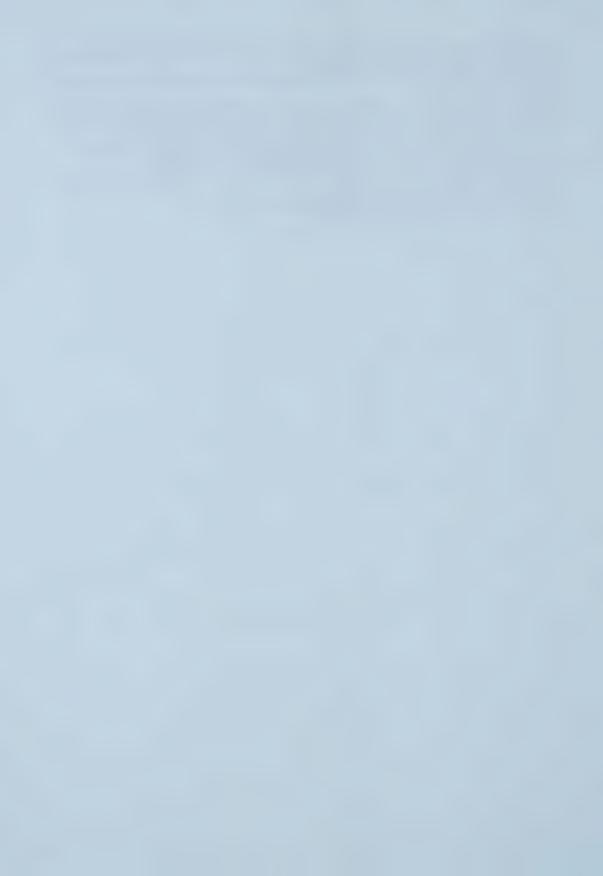
- 1. Enter CAT ID data of the GC Analysis worksheet; i.e. autosampler rack position, a number between 1 and 23, the corresponding CAT ID, and the type of CAT, standard (std) or field sample (unknown,). Every run must have all 9 standard CATs necessary to construct a standard curve. Also every one must have at least one(1) lab blank and/or field blank. A Run will have then either 12 or 13 unknown CATs.
- 2. Remove the cam adjusters and the top plate from the rack
- 3. Loosen the C-clamps on the bottom plate of the rack
- 4. Use gloves. Apply a small amount of silicone grease to a Q-tip (or equivalent). Carefully and lightly use the Q-tip to apply the grease to the red silicone O-rings in the bottom plate. Clear any visible excesses. The grease facilitates the insertion of the CATs into the O-rings. The O-rings on the top plate must be greased only once every week.
- 5. Remove the cap from the plain unnumbered side of each CAT and insure that the top cap is not very tight.
- 6. Insert the 23 CATs with the ID facing up, through the heating coils into the O-rings according to the sequence on the worksheet. Press firmly but do not force which can cause breakage. Adjust the C-clamps firmly but not too tightly.
- 7. Replace the top plate carefully; line up the top of the CATs with the wells on the top plate and press it firmly down to seat barely the CATs.
- 8. Insert the cam-adjusting holding the arm in the 3 o'clock position. Replace and finger-tighten the nuts on the cam-adjusting screw.
- 9. Rotate the cam-adjusting arms counter clockwise slowly and carefully to set the CATs and seal the O-rings. Use care so as not to break anything.
- 10. Attach the bungee cord to the cam-adjusting arms to prevent the arms from loosening.
- 11. Check the autosampler's LED reading for position. If not (00) use the toggle switch on the respective controller to reset it to 0.00

GC Procedure

1. Check the A and B pressures on the right side of the instrument. The gauges should be pointing to the preset marks of 42 psi and 80 psi. The carrier gas pressure must be 80 psi as measured on the tank's regulator gauge.



- 2. Insure that the integrator is in BASIC mode. Press "R" (for run) then "ENTER". Follow the instruction on the integrator. When it prints "start pending" PROCEED.
- 3. Place the recorder ON/OFF toggle switch in the ON position. Activate the timer by pressing "CIRCUIT", "1", "ON", "PROGRAM", "1", "ON".
- 4. On the left side of the GC, press "SCHEDULE". Set the mode for "SINGLE PASS", if necessary. Repeatedly press "ENTER" to get to line 1 and enter "2" for the method # and "24" for the number of injections. Press the "ENTER" button, then "INSTRUMENT STATUS" A. Finally press "START" to initiate the run.
- 5. The run will go for about 3.5 hours. Check the progress frequently to make sure the instruments are functioning properly and the area counts for standards and blanks are in the proper range.
- 6. When the run has been completed, remove the strip chart and the integrator chart and place them in a labelled file folder along with the GC analysis worksheet.
- 7. Remove the CATs from the autosampler by reversing the procedure above.
- 8. Recap the CATs and set them in the bin for cleaning.



Appendix A. Parameters for GC.

```
Oven temperature = 130 °C.
Oven temperature limit = 150 °C.
Run time = 8.5 minutes
```

Inj A temperature = 200 °C. Inj B temperature = 200 °C. Ion temperature (ECD) = 250 °C. TCD temperature = OFF

Detector = 4 (ECD)
Range 10 (only two choices, 1 or 10)
Attenuation = 32 (0.1,1,2,4,8,16,32,64,128,256,512,1024)
AutoZero A ON
AutoZero B ON

Relay Settings:

Time	Relays ON	Relays OFF
0.01	3456	1278
0.25	12	
0.41		5
2.01	7	16
2.02		7
4.01	8	23
4.61	3	8

Appendix B. Parameters for Integrator operational settings.

Appendix C. Program of Integrator data reduction.

Appendix D. Program for Chrontrol Timer which controls the recorder pens.

To reset, the timer-controller should be disconnected from the wall outlet for at least one minute. Then perform the following key entry procedures:

TIME
ENTER
1
ENTER
CIRCUIT
1
OFF
INTERVAL
3
4
5
ENTER
ENTER
ENTER
ENTER

TIME



To test the timer operation, first set up the program by pressing

TIME
ENTER
I
ENTER
CIRCUIT
I
ENTER
OFF

INTERVAL

after INTERVAL press

0 SEC 5 ENTER TIME

To set the timer for a 5 second shutdown. To test, press

CIRCUIT I ON

and the circuit 1 indicator lamp should light.

Then press

PROGRAM I ON

At which time there should be a barely noticeable blink of the display; after 5 seconds, there should be an audible clicking sound simultaneous with the circuit 1 lamp light extinguishing. If this does not happen, then try reentering the program. When the test is successful, repeat the key entry procedure above entering 345 instead of the SEC 5 after the INTERVAL.

Calculations

Standard Curve

There is a spreadsheet template for entering the area counts from the integrator. It is straightforward and produces the calculated data for the unknowns. The replacement equations used in the template are very complex and it is suggested not to alter them. They are designed to produce a point-to-point fit for the standard curve. The curve's shape tends toward a quadratic as long as the amount of PMCH does not exceed about 400 picoliters.



Note that the PMCH standard curve is not linear and so linear regression analysis (least squares analysis) cannot be used successfully across the entire range of interest.

Short of the template, one can devise their own spreadsheet as follows. Let the pl of PMCH from the standard CATs be the Y values and the area counts from the integrator be the X values. Enter these values in a spreadsheet which can perform either a quadratic fit or a point-to-point linear fit (sometimes termed a piecewise fit). Cubic may also work. The spreadsheet should be able to draw the standard curve and calculate the values of X for given values of Y.

Preparation of Standard Curve

From the PMCH source permeation rate and the measured nitrogen flow from the PMCH generator, calculate the PMCH concentration (pl/µl) of the standards used as described earlier. Enter this value into the designated cell in the spreadsheet. Enter the corresponding area counts into the designated cell(s) in the spreadsheet.

[Alternatively, multiply the PMCH concentration by the percent of PMCH in the reagent (usually 90%). Multiply this by the volume(µl) of gas used for each standard to get the total amount of PMCH.]

Calculation of PMCH in Unknowns

For the complete run, enter the sample (standard) ID and the corresponding integrator area counts into designated cells in the spreadsheet. SHOW AN EXAMPLE Now, the final data appears in the adjoining cells and the standard curve can be seen in the nearby chart.

The concentration of PMCH in unknowns is calculated from the unknown area counts, the amount of PMCH in the standard with next least area counts, and the slope for the corresponding area count point on the standard. The slope is obtained either from the point-to-point fit or the quadratic equation. IS THIS CLEAR OR CONFUSING?

Organization of Files and Worksheets SHOW EXAMPLES

Worksheets Source Permeation Rates Cleaned CATs QA'd CATs Standard CATs

Files

GC Analyses Sources CATs Clean QA'd

Computer

Sources Templates Clean and Run Standards Special Runs Data and Results



Shipping Procedures

Sources

Sources and CATs should never be transported together nor on the same day. Sources should be shipped in resealable plastic bags in a box within a box. Their value is usually listed at \$0.50 to \$1.00 each. Paper records should be maintained showing what carrier, when, and the airbill or waybill number.

CATs

CATs are in resealable plastic bags with charcoal protection. These bags must be placed with charcoal paper or equivalent in a box within box for shipping. The declared value is \$1.00 each.

Boxes for shipping should be adequately cushioned and taped with 3" postal tape or equivalent,

Field Sampling

Introduction

As with any chemical determination, the data are only as good as the sample. PFT AER is a passive technique operating in a possibly heterogeneous sampling theatre. So, attention to numbers of sources and CATs as well as careful placement of PMCH sources and CATs are very probably the most important parts of the AER protocol.

Determination of the Number of Sources

The number of sources is determined by rearrangement of Equation

$$AER = (N * R_{perm} * R_{CAT} * T_{CAT})/(V_{pMCH} * V_{bones})$$

and obtaining:

$$N = [AER * (V_{PMCH} * V_{house})] / (R_{Perm} * R_{CAT} * T_{CAT})$$

where

N = number of PFT sources used

R_{Perm} = PFT permeation rate in ng/min

 $R_{CAT} = CAT$ collection rate in liters/hr = 0.00838

 $T_{CAT} = CAT$ exposure time in min

V_{PMCH} = picoliters of PMCH found on CAT (GC analysis)

 V_{house} = house volume in cubic feet

and conversion factors:

60 min/hr

28.3 lit/cubic foot

1,000,000,000 ng /gm

1000 picoliters/nanoliter

PMCH molecular weight = 350 gm/mole or ng/nmole

PMCH molecular volume = 24.45 lit/mole or nl/nmole

A desirable amount of PMCH to collect on a CAT is in the range of 20-100 μ l. The sampling time is determined according to convenience, subjective assessment, and consideration of other simultaneous sampling.



To calculate the number of sources needed in a given location, using an estimate of 0.2 air changes per hour and an average $R_{\text{perm}} = 300 \text{ ng/min}$ and a house volume of 6,048 cubic feet, with an exposure of 24 hours, then to collect 25 pl of PMCH,

$$N = [AER * (V_{PMCH} * V_{bouse})] / (R_{Perm} * R_{CAT} * T_{CAT}) \text{ or }$$

 $N = [0.2 \text{ air changes per hour * (25 pl * 6048 cubic feet * (28.3 lit/cubic foot)}] / (300 ng/min * {24.5 nl/350 ng} * (1000 pl/nl) * 0.008308 lit/hr * 24 hr * 60 min/hr)$

N = 2 sources

Determination of the Number of CATs

The number of CATs to be employed is determined according to the type of information desired. For average air exchange rate, as few as 1 or 2 CATs can be used if optimally placed. For a more accurate measure of average air exchange rate, CATs may be located in every room in the house or building. If one wants to know the AER for a given room, then 2 or more CATs may be placed there as well as a PMCH source. This can get very complex very quickly when one considers that air exchange occurs not only with the outdoors through window areas, but also within the home through the door. In this case it is best to employ another tracer, say PDCH, in a nearby hallway to determine the rate of inflow of air into the target room from the hallway, i.e. some measure of the air exchange between hallway and target room. This should be complemented by placing CATs in the hallway to measure the PMCH and thus get an independent measure of outflow of air into the hallway. Some of these issues are discussed in detail references 1 and 2.

In addition to the above, there should be at least 10% duplicate CATs and 10% Field Blanks.

Locating Sources and Cats

As can be seen from the immediately preceding paragraph, the optimal positioning of sources and CATs is necessary to obtain the most meaningful AER data. A complete discussion is beyond the scope of this document.

Some general considerations can be stated however. Sources and CATs should be placed in area which allow relatively free but not forced movement of air. CATs should be as close as reasonably possible to the breathing height for both sitting and standing and be in an area which is representative of where occupants sit or stand, and representative of the AER in that room. This is obviously a very subjective judgement in the absence of additional instrumentation. Sources should be in an area that allows the tracer to disperse evenly and be transported in the dwelling to all locations which influence the AER.

Among the areas to avoid are windows and doors where there are strong drafts or winds, stairways which have increased vertical air movement due to thermal effects, adjacent to walls or in "cubbyholes", and away from sources of heat and cold, and appliances such as refrigerators and dehumidifiers which contain Freons, a potential interferent in the analysis.

It is good for CATs to be suspended if possible, or placed on a flat surface with the exposed end protruding beyond the end of the surface, e.g. a table or mantle or bookcase or bureau.



Deploying Sources and CATs

The sources are contained in polyurethane blocks and should never be touched or removed. There is one source per block. Sources are sent to the field I resealable plastic bags. They are never shipped or transported together anywhere with CATs particularly regarding the sampling location. Sometimes some charcoal is placed with the sources. The charcoal absorbs the PMCH so that it cannot escape or contaminate anything. Every block has an external ID which matches the sources contained within. Sources can be secured by taping (removable type adhesive tape) or tying with a string (using the available hole in the block). Dental floss is a very convenient material for the latter. Orientation, though not the most important issue, should still be considered: try to secure so the ID is in readable position. Record the date, time, and location (include a sketch) on the sample data sheet.

The CAT samplers are packaged 5 to a resealable plastic bag; they should always be protected by charcoal paper, tea bag, or equivalent. CATs are set out 24 hours or longer after the sources have been deployed. They can be taped (removable type adhesive tape) or secured with a wire of plastic tie, or tied with dental floss. They should never be closer than six (6) feet from a PMCH source. Once the location is selected and the CAT secured, the sampling CAT is "activated" by removing the cap on the numbered end and positioning it by having the open end facing down, to minimize collection of particles. Record the date, time, and location of the CAT on the sample data sheet.

Field Blanks

Field Blanks (CATs) are transported to the sampling location, and treated identically to unknowns except they are opened then immediately closed. They should be protected by charcoal paper or tea bags, replaced in the plastic bag, and left at the house if convenient, otherwise taken to the local field office or equivalent where there is no source of unprotected PMCH.

Duplicates

Duplicate CATs are used to establish precision. They are prepared and treated identically to the main CAT. They should be placed next to the main CAT within about 3-6 inches. Both duplicates and Field Blanks should be recorded on the sample data sheet.



Appendix 4: Survey Instruments

A4.1	Household Characteristics Questionnaire (Q1)	156
A4.2	Personal Exposure and Activity Questionnaire (Q2)	163
A4.3	Household Activity Questionnaire (Q3)	166
A4.4	Time-Activity Log	169



Ft. McKay Air Quality Study QUESTIONNAIRE: HOUSEHOLD CHARACTERISTICS (Q1)

Interviewer:

	Date:
Title of Project:	COMMUNITY SAMPLING OF PARTICULATE MATTER, SULPHUR DIOXIDE AND VOLATILE ORGANIC COMPOUNDS IN FORT McKAY
Principal Investigator	r:Warren Kindzierski University of Alberta
Co-Investigators:	Fort McKay Industrial Relations Corporation
Field Investigators:	Russ Miyagawa, Bettina Mueller, Sunita Ranganathan University of Alberta Phone: 492-8548
Instructions:	
will be used for res	otained by this questionnaire will be held in strict confidence and search purposes only. All results will be summarized for groups of ation regarding individual persons will be released without the vidual.

Your answers help to determine things about your home that may affect indoor air quality. Before you answer a question as "unknown", please refer to the glossary

of terms for unfamiliar words or ask your interviewer for help.

Thank you for your co-operation.

Sample #:



Α.			ticipant Idei	tification	<u>:</u>						
1.	Partici	pant Name	:								
2.	Partici	pant Phone	No.:								
3.	Street	Address, P	O. Box								
4.	City/H	amlet:									
<u>B.</u>	House	hold Habi	tants:		A						
5.	Who lives in the house?										
	Name		Sex (M/F)	Age*	Smoker (Y/N)	Occupation .					
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
* If	exact age	not given,	please select	a range fro	om the following:	0-12, 13-17, 18-30, 31-					
40,	41-50, 51-	60, 60+									
Are	there any	pets in y	our househo	ld?							
	yes			no							
If y	es, what k	ind of pet	s do you hav	e?							
	dog	cat		other							
<u>C.</u>	Type	of House									
6.	Which	best desc	ribes your h	ome?							
		a mobile	home or traile	er							
			nily house det	ached fron	n						
7.	How t	any other ig is the h	house louse, withou	it the base	ment?						
			feet, or			check box if estimated					



8.	Do you have a finished baseme	ent?					
	yes] r	10				unknown
9.	How big is the basement?						
	square feet, ors	quare	metres				
	check box if estimated						
10.	In what year was the house or	iginal	ly built	?			
11.	Is there an unpaved driveway	on yo	ur proj	perty?			
	yes] r	no				•
12.	Is there a garden on your prop	perty					
	yes] [no				
13.	Do you have an outdoor barbo	ecue, 1	firepit o	or burnt	arrel?		
	yes] 1	no				
14.	Do you have a smokehouse?						
	yes] [no				
15.	While you are awake, in which	h area	a of you	r home	do you	spend	MOST of your
	time?						
	bedroom] 1	kitchen				
	spare room] 1	living ro	oom			
	dining room] '	rec roon	n			
	other						
<u>D.</u>	Heating, Ventilation, and Air	Cond	itioning	<u>System</u>	<u>15:</u>		
16.	Does the house have an air co	nditio _	ner?			_	
	yes] 1	no	_	Ĺ	١	unknown
	If yes, what type?	entral		ro	oom		
	If it is a room air conditioner, w						
17.	Does the house have any fans	for ex	ktra ven	itilation	?	_	
	yes]	no		L	ل	unknown
	If yes, what type(s)?						
	portable fan ceilin	ng fan		b	athroon	n fan	
	Location(s)?						•



18.	Does the house have an air purification system installed?						
	yes	no no			unknown		
	If yes, what type?						
19.	Does the house have any	y range hoods,	fume hoods?				
	yes	no no			unknown		
	If yes, where is it?		Α				
	Where does it vent to?						
	outside	inside inside			unknown ·		
20.	Have you had your gas	pipes/gas appli	ances checked	l for leak	s?		
	yes	no no			unknown		
	If so, when?						
21.	How do you heat your	nome? Where a	re the heaters	located?			
	Type of System	Primary	Second	Third	Location		
	forced air furnace						
	gravity furnace						
	radiant heat - wall						
	radiant heat - floor						
	fireplace						
	stove						
	room heater						
	portable heater						
	other						
22.	What type of fuel do yo	ou use?					
	Type of fuel	Primary	Second	Third			
	natural gas						
	fuel oil						
	electricity						
	kerosene						
	wood						
	other						



23.	Do you keep the house at the same temperature all the time?									
		yes		no		unknown				
24.	Does the heating system have a combustion air supply?									
		yes		no		unknown				
25.	Does t	the heating system ha	ive a fr	esh air return?						
		yes		no		unknown				
26.	Do yo	u use a humidifier								
		room humidifier		attached to furnace		no				
		unknown								
27.	Do yo	u have a sump pump	?							
		yes		no		unknown				
E.	Attac	hed Structures:								
28.	Does	the house have any a	ttached	structures?						
		yes		no		unknown				
	If yes.	, what type(s)?								
		garage		shed/shop		porch				
		greenhouse		other						
	If no	then go to Question 3	3.							
29.	Do yo	u start your vehicle i	n the g	arage						
		yes		no		unknown				
30.	Does	the attached structur	e(s) ha	ve a door that opens i	nto the	house?				
		yes		no		unknown				
	If yes	, is this door(s) usual	ly left o	pen or closed?						
		yes		no		unknown				
31.	Does	the attached structur	e have	a heating system?						
		yes		no		unknown				
	If yes	, what type?				_				
	Please use the categories listed in question (21,22).									



<i>32.</i>	Does the attached str	ucture have a	any ventilation	or exhaust	system(s)?				
	yes		no		unknown				
	If yes, what type?								
	window/overhead	door ex	haust system	☐ fan					
	If exhaust, where do	es it vent to?	outside	e 🗌	inside				
F.	Household Sources	of VOCs, PM	, SO ₂ :	,ì					
33.	Are all of your household appliances (cooking stove, hot water heater, clothes								
	dryer, etc.) electric?	If no, please	complete the b	elow table.	•				
	yes		no		unknown				
		Type of Fue	el (🗸)						
	Type of Appliance	natural gas	other	lo	ocation				
			(specify)						
	cooking stove								
	hot water heater								
	clothes dryer								
	other								
			<u> </u>	I					
34.	Do you ever use the	cooking stove	for heating yo	our home?					
	yes		no		unknown				
35.	Is the clothes dryer	vented to the	outside?						
	yes		no		unknown				
36.	Do you have carpet i	in your home	?						
	yes		no		unknown				
37.	How much carpet w	ould you gues	ss your home h	ias?					
b.	<25%	25 to 509	% 🗌 51 to 759	%	>75%				
38.	Has any part of the	house had car	pet installed v	vithin the pas	st year?				
	yes		no		unknown				
	If yes, than within p	ast: 3	months		6 months				
	Where was it installed	1?							



39.	Do people smoke inside the house or any of the attached structures?								
		yes			no			unknown	
Com	ments:								
				End of	Questio	nnaire			



FORT MCKAY AIR QUALITY STUDY

Personal Exposure and Activity Questionnaire (Q2)

House #: _	Interviewer:
Participan	t Name://
pas	you have your drapes, carpet, or furniture professionally-cleaned during the t 24 hours? Yes \text{No}
	you vacuum your home during the past 24 hours? Yes \text{No}
	re any windows left open in your home during the past 24 hours? Yes \text{\subset} \text{No}
	ve you used tobacco, in any form, during the past 24 hours? Yes (GO TO QUESTION 4a)
b)	☐ Cigarettes ☐ Cigars ☐ Pipe Approximately how many cigarettes did you smoke during the past 24 hours?
	yes (GO TO QUESTION 5a) No (GO TO QUESTION 6)
a)	Which of the following tobacco products have been smoked inside your home in the past 24 hours? ☐ Cigarettes ☐ Cigars ☐ Pipe
b)	Approximately how many cigarettes/cigars/pipes were smoked (by yourself or by others) inside of your home in the past 24 hours?
enc	re you exposed to second-hand tobacco smoke during the past 24 hours (in closed area with active smokers for more than 15 minutes)? Yes (GO TO QUESTION 6a)
a)	For how long were you exposed to second-hand smoke during the past 24 hours?



7.	during Yes	the past 24 hours? Is (specify below)	f yes, please sp	noke (forest or camp fires, smoke houses, etc.) please specify the source(s) of the smoke. No								
8.		y food been cooked										
	☐ Ye	s (GO TO QUESTIO	N 8a) 🔲 No	(GO ŤO (QUESTION	9)						
	a)	Has any food been f	ried inside vot	ır home in	the past 24	1 hours?						
		☐ Yes	□ No		•		•					
9.	Have y	ou used or worked v	with insecticide	es, pesticid	les, or herb	icdes in th	e past 24					
	☐ Ye	s	□ No)								
10.	specify	ou operated any gas the appliance or too s (specify below)		uel.	tools in the	past 24 ho	ours? If yes,					
	1. 2. 3. 4.	Appliance/Tool	Fuel									
11.				led near a								
Please	provide	details of any trips y	ou have made:									
	Trip	Type of Vehicle	Duration	Windo	ws	Heavy T	raffic?					
	1.		min	open \square	closed	yes□	no					
	2.		min	open \square	closed	yes□	no					
	3.		min	open \square	closed	yes□	no					
	4.		min	•	closed□	yes□	no					
	5.		min		closed	yes□	no					
	6.		min	open \square	closed	yes□	no					



12.	Have you worked at or visited any of the hours? (Check all that apply)	followi	ng businesses during the past 24
	Worked Visited Painting Chemical/plastics plant Service station/garage Wood processing plant Hospital	Worked	Visited ☐ Dry cleaning ☐ Petroleum plant (Oil sands) ☐ Furniture refinishing/repair ☐ Printing ☐ Renovations/construction
13.	Have you performed any of the following (Check all that apply)		
	☐ Metal work	☐ We	elding
	Plumbing	☐ Pla	astics work
	Automotive or other mechanical repair	☐ Au	to body repair
	☐ Painting	☐ GI	uing/caulking
	☐ Furniture refinishing/repair	☐ Flo	oor waxing/strippping
	☐ Other renovations/redecorating – specifi	y:	
	☐ Used degreasers	☐ Us	ed air fresheners/deodorizers
	☐ Used other cleaning products – specify:		
	☐ Scale model building		her hobbies/craftwork
	Other activities which may have led to e	exposure	e to chemicals:
14	Disease in directs come other events during t	hic time	a portiod which may have led to
14.	Please indicate any other events during t exposure to chemicals or airbourne pollu		e period which may have led to
	:		
	-		
	END OF QUEST	TIONN	AIRE

24-Hour Personal Activty Questionnaire (Q2)



FORT MCKAY AIR QUALITY STUDY Household Activity Questionnaire (Q3)

Hous	se #:	Interviewer:
Parti	icipant Name:	///
1.	past 4 days?	et, or furniture professionally-cleaned during the
	☐ Yes	□ No
2.	Did you vacuum your home dur	ring the past 4 days?
3.	Were any windows left open in	your home during the past 4 days?
4.	Has anyone smoked tobacco ins ☐ Yes (GO TO QUESTION 4a)	ide of your home in the past 4 days? No (GO TO QUESTION 5)
	Which of the following to ☐ Cigarettes ☐ Cigars	obacco products were used in the past 4 days? □ Pipe
	b) Approximately how man inside of your home in the	y cigarettes were smoked (by yourself or by others) he past 4 days?
5.		camp fires, smoke houses, etc.) present in or he past 4 days? If yes, please specify the source(s) of
	Yes (specify below) Specify:	□ No
6.	Have you used or worked with your home in the past 4 days?	insecticides, pesticides, or herbicdes in or around
	☐ Yes	□No
7	Have you operated any gas-pow the past 4 days? If yes, specify to Yes (specify below)	vered appliances or tools in or around your home in the appliance or tool and type of fuel. No
	Vehicle/Appliance/Tool 1 2	Fuel
	3.	



Did you use a portable fan or humio Yes (specify location below) Where?	difier in you	r home in the p	past 4 days?
Did you use your clothes dryer in th	ie past 4 day	s?	
Have you performed any of the follouring the past 4 days? (Check all t		ties in or aroui	nd your residence
☐ Metal work		□indoor	□outdoor ,
☐ Welding		□indoor	Outdoor
Plumbing		□indoor	Outdoor
☐ Plastics work		□indoor	Outdoor
☐ Automotive or other mechanical re	epair	□indoor	Outdoor
☐ Auto body repair	•	□indoor	Outdoor
☐ Painting		□indoor	Outdoor
☐ Gluing/caulking		□indoor	Outdoor
☐ Furniture refinishing/repair		□indoor	Outdoor
☐ Floor waxing/strippping		□indoor	Outdoor
Other renovations/redecorating –	specify:	□indoor	Outdoor
Used degreasers		□indoor	Outdoor
☐ Used air fresheners/deodorizers			
☐ Used other cleaning products – sp	ecify:	□indoor	Outdoor
☐ Scale model building		□indoor	Outdoor
Other hobbies/craftwork		□indoor	Outdoor
Other activities which may have l	ed to exposu	e to chemicals:	



11.	Do you have any of the following items in or around your? Where is it stored?
	Did you use it recently, and if so where? Please complete the below table.

Item	Do	Storage location?	Recent	Where was recent use (if
	you	(specify floor and room)	use?	different from storage)?
	have?		(n/d/wk)	(specify floor and room)
	(y/n)			
Gas, oil			ı,	
Propane				
Other fuels				•
Vehicles				
Rec. vehicles				
Pesticides/				
Fertilizers				
Paint or				
varnish				
Solvents				
Glues				
Dirty work				
clothing				
Clean/disinf.				
Agents				
Air deodorant				
Mothballs				
Cosmetic/hair				
products				
Aerosol spray				
Office equip.				

Please indicate any other events during this time period which may have									
	exposure to chemicals or airbourne pollutants:								

END OF QUESTIONNAIRE



FORT MCKAY AIR QUALITY STUDY Time-Activity Log

Sample No.: Date:

1. Record the approximate starting and ending times for each activity during the sampling period.

2. Place a check mark (✓) in the appropriate location box.

3. Record a general description of the activity and more specific information about the location (e.g. indicate the room in the home in which the activity occurred).

DESCRIPTION OF ACTIVITY/LOCATION										
OUTDOORS	Other									
OUTD	Vehicle or Roadway									
	Other									
INDOORS	Work or School									
	Home									
Ш	0									
TIME	From									

- 1
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- 1
- 1
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Time Activity Log

8/27/99



Appendix 5: Field Log Data Sheets

A5.1	VOC Field Data Log Sheet	171
A5.2	Air Exchange Data Sheet	172
A5.3	Floor Plan	173
A5.4	VOC Sampling: Chain-of-custody Form	174



Fort McKay Air Quality & Exposure Study: VOC Field Data Log Sheet

d by:		Personal (24 h)	place sticker betw				place attcker bere				: place sticket hurv				place sticker here	
Received by:		Indoor (24 h)	place sticker bere				placo sticker bere				place slicker here				place sticker bere	
Start Date:	End Date:	Indoor (96 h)	place xiickei here				place slicker berv				place sticket bere				place Micker here	
	Submitted by Field Team Members:	(Judoor (96 h)	place sticker bere				place sticker here				place sticker here				place sticker here	
Participant ID #:	nitted by Field	A to wind to the manual beautiful to the second	Sampler ID #:		Start Lime:	Comments:	Sampler ID #:	Start Time.	End Time:	Comments:	Sampler ID #:	Start Time:	End Time:	Comments:	Sampler 1D #:	. Comments:
Partic	Subn		Sample	A CALL OF THE PARTY OF THE PART			Replicate #1				Replicate #2				Blank	



Air Exchange Data Sheet

		_		T	T				1		1	1	_		T			1
		Location									Location							
	ted	Time								ted	Time							
	Collected	Oate	Dago							Collected	Date							
	ed	J. B.	20111							pe pe	Time							
	Deployed		Date							Deployed	Date							
			#01								# 0							
House #:			Source	,-	0	0	2	4	r.	•	100			2	4	1	28	blank

FLOOR PLAN: Skech home and indicate location of all sources and CATs.



Fort McKay Air Quality Study

Sampled By:	
House #:	
Date:	

FLOOR PLAN:



louse #:_		g: Chain-c	of-cust	ody F	orm		
Sampler II		(place label here) .	Se	erial #:		
Sample Tv	rpe (circle):	OUT	IN96	IN24	PERS	BLANK	MET
Rel'd by	Rec'd by	Date	Time	11424		Operation	MCI
			11111			орогилоп	
	1						`
	, ,						
			<u> </u>				
Sampler II	D#:	(place label here)	Se	erial #:	· ,	
	pe (circle):	OUT	IN96	IN24	PERS	BLANK	MET
Rel'd by	Rec'd by	Date	Time			Operation	
			-				
Sampler II Sample Ty	O#: /pe (circle):	(place label here) IN96	Se IN24	erial #:	BLANK	MET
	Rec'd by	Date	Time			Operation	
	-						
Sampler II	D#:	(place label here)	Se	erial #:		
	ype (circle):	OUT	IN96	IN24	PERS	BLANK	MET
Rel'd by	Rec'd by	Date	Time			Operation	
,							
			1				

Voc-coc

__ of __



Appendix 6: Raw Analytical Results

A6.1	Blank Results	176
A6.2	Fall Analytical Results	177
A6.3	Winter Analytical Results	183



Table A6-1 Fall and Winter Analytical Results: Blank Badges

Hexano Egulation Heyare Fenerane Elliny-land Morane Elliny-land According Signature Elliny-land Morane According Signature Processor Processor <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th>Ana</th> <th>Analyte Mass (ng)</th> <th>(ng)</th> <th></th> <th></th> <th></th> <th></th> <th></th>							Ana	Analyte Mass (ng)	(ng)					
Fall 150 150 150 150 150 150 150 1	I	exane	2- Butanone	3-Methyl- hexane	Benzene	Heptane	Toluene	Octane	Ethyl- benzene	m,p- Xylenes	Nonane	o-Xylene	Decane	Limonene
150								Fall						
200 150 315 0 </td <td></td> <td>420</td> <td>150</td> <td>0</td> <td>0</td> <td>0</td> <td>765</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td>		420	150	0	0	0	765	0	0	0	0	0	0	0
270 0 150 0 885 0 </td <td></td> <td>300</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>315</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td>		300	0	0	0	0	315	0	0	0	0	0	0	0
10 10 10 10 10 10 10 10		360	270	0	150	0	885	0	0	0	0	0	0	0
0 0 570 0		195	0	0	0	0	315	0	0	0	0	0	0	0
0 0 0 975 0		360	0	0	0	0	570	0	0	0	0	0	0	0
10 10 10 10 1156 1156 10 10 10 10 10 10 10 1		645	0	0	0	0	975	0	0	0	0	0	0	0
112 112 112 113 114 115		480	0	0	0	0	585	0	0	0	0	0	0	0
Mathematical Colored		600	0	0	390	0	1125	0	0	0	0	0	0	0
Mathematical Colored		930	0	0	0	0	750	0	0	0	0	0	0	0
Winter Winter Minima Minima<		099	0	0	0	0	1110	0	0	0.	0	0	0	0
0 0 360 360 0 <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>Winter</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>								Winter						
0 0 0 315 0		705	0	0	0	0	360	0	0	0	0	0	0	0
0 0 0 540 0		195	0	0	0	0	315	0	0	0	0	0	0	0
0 0 495 0		255	0	0	0	0	540	0	0	0	0	0	0	150
4 6 720		510	0	0	0	0	495	0	0	0	0	0	0	0
0 0 0 1005 0 165 0 165 0<		810	0	0	0	0	720	0	0	0	0	0	0	0
0 0 0 945 0 150 0 <td></td> <td>585</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>1005</td> <td>0</td> <td>0</td> <td>165</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td>		585	0	0	0	0	1005	0	0	165	0	0	0	0
0 0 0 465 0		330	0	0	0	0	945	0	0	150	0	0	0	0
0 0 0 390 0		0	0	0	0	0	465	0	0	0	0	0	0	165
0 0 0 720 0 165 0 <td></td> <td>150</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>390</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td>		150	0	0	0	0	390	0	0	0	0	0	0	0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		285	0	0	0	0	720	0	0	165	0	0	0	195
0 0 0 900 0		225	0	0	0	0	009	0	0	0	0	0	0	0
0 0 0 885 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		0	0	0	0	0	006	0	0	180	0	0	0	0
0 0 0 0 435 0 0 0 0 0		375	0	0	0	0	885	0	0	150	0	0	0	0
		450	0	0	0	0	435	0	0	0	0	0	0	0



Table A6-2 Fall Sampling Results

					Ë	Time-Weighted Average Concentration (ug/m³)	nted Ave	rage Co	ncentrati	on (ua/n	(81			
Sampler ID	House ID	HEX	BUT	MET	BEN	HEP	TOL	OCT	ETH	MPX	NON	×-o	DEC	LIM
					Fall Inc	Fall Indoor (24-hour) Samples	nour) Sa	mples						
6393	1	7.6	3.7	0.0	5.1	0.0	6.5	0.0	0.0	4.9	0.0	0.0	0.0	47.5
6548	2	15.5	8.5	7.5	6.1	7.1	46.6	0.0	4.5	13.2	0.0	4.5	0.0	8.9
6219	3	0.0	10.0	10.0	19.2	12.9	22.1	19.7	4.3	9.8	0.0	0.0	0.0	48.7
6442	4	2.7	0.0	0.0	3.5	0.0	11.0	0.0	0.0	0.9	4.6	0.0	0.0	13.4
6416	5	0.0	3.8	0.0	6.4	0.0	5.4	0.0	0.0	4.3	0.0	0.0	10.1	9.5
6389	9	0.0	2.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.3
6418	7	0.0	10.7	5.4	14.0	0.0	11.7	11.0	0.0	6.9	0.0	0.0	0.0	11.9
6446	8	18.5	0.0	5.3	4.3	0.0	50.3	0.0	0.0	7.9	0.0	0.0	0.0	63.1
6437	6	6.6	1.1	0.0	3.2	0.0	8.9	0.0	0.0	4.0	0.0	0.0	0.0	11.9
6541	10	0.0	0.0	0.0	4.4	0.0	24.0	0.0	0.0	6.1	4.3	0.0	0.0	22.3
6538	11	0.0	0.0	5.0	15.7	5.8	16.3	0.0	0.0	6.9	0.0	0.0	0.0	145.5
6546	11	0.0	0.0	0.0	18.8	2.0	5.7	0.0	0.0	5.7	0.0	0.0	0.0	147.0
6556	11	0.0	0.0	0.0	14.7	4.6	3.6	0.0	0.0	5.3	0.0	0.0	0.0	150.0
6533	12	0.0	0.0	0.0	0.0	0.0	14.3	0.0	0.0	10.2	0.0	4.3	0.0	4.6
6438	13	19.0	0.0	8.9	14.4	8.3	38.6	3.2	9.4	35.9	0.0	13.2	0.0	17.5
6486	14	0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.0	4.8	0.0	0.0	0.0	6.1
6493	14	0.0	0.0	0.0	3.0	0.0	2.4	0.0	0.0	4.0	0.0	0.0	0.0	5.8
6505	14	0.0	0.0	0.0	0.0	0.0	2.8	0.0	0.0	0.0	0.0	0.0	0.0	5.4
6547	15	0.0	7.9	0.0	9.9	0.0	38.2	0.0	0.0	7.8	0.0	0.0	0.0	36.0
6445	16	24.3	0.0	6.3	5.4	7.7	39.3	8.4	6.2	21.4	4.8	8.2	9.5	77.0
6440	17	4.9	0.0	0.0	3.1	0.0	25.0	0.0	0.0	6.2	0.0	0.0	0.0	27.9
6496	18	0.0	9.8	0.0	9.7	0.0	18.5	0.0	4.3	11.0	0.0	0.0	0.0	71.8
9689	19	9.4	12.6	0.9	3.5	6.4	23.9	7.4	0.0	0.0	0.0	0.0	0.0	12.3
6467	20	2.8	0.0	0.0	3.3	0.0	22.9	0.0	0.0	6.2	0.0	0.0	0.0	14.9
6403	21	0.0	4.6	0.0	6.7	0.0	13.8	0.0	0.0	5.7	0.0	0.0	0.0	10.7



Table A6-2 Fall Sampling Results (continued)

					Ţ	Time-Weighted Average Concentration (µg/m³)	nted Ave	rage Col	ncentrati	on (ug/n	13)			
Sampler ID	House ID	HEX	BUT	MET	BEN	HEP	TOL	OCT	ETH	MPX	NON	×-0	DEC	LIM
6499	22	0.0	0.0	6.1	5.5	7.1	33.2	7.0	3.8	12.1	0.0	4.9	0.0	72.3
6391	23	2.8	0.0	0.0	5.1	0.0	12.8	12.4	0.0	6.8	0.0	0.0	0.0	13.4
6411	24	0.0	4.4	0.0	0.0	0.0	4.4	0.0	0.0	4.6	0.0	0.0	0.0	6.3
6449	25	1.9	0.0	0.0	9.3	0.0	21.8	4.0	3.9	10.0	0.0	0.0	0.0	206.3
6502	26	68.1	0.0	20.9	17.0	18.6	45.1	3.9	22.5	94.0	0.0	31.8	0.0	22.0
6501	27	11.1	6.3	0.0	9.7	0.0	32.5	0.0	0.0	9.5	0.0	0.0	0.0	15.3
6522	28	7.2	8.1	0.0	7.4	4.0	18.4	0.0	0.0	6.5	0.0	0.0	0.0	12.9
6385	29	1.7	6.8	0.0	5.3	0.0	44.0	0.0	0.0	10.3	0.0	4.6	26.3	34.4
6517	30	4.6	0.0	0.0	3.5	0.0	14.3	0.0	0.0	5.4	0.0	0.0	0.0	106.5
					Fall Indoor	oor (96-h	(96-hour) Samples	mples						
6422	1	1.1	0.0	1.1	4.3	0.0	8.4	0.0	1.2	4.0	0.0	1.3	0.0	22.4
6515	2	17.8	6.1	3.3	4.6	0.0	10.2	1.4	2.6	8.0	2.0	2.9	0.0	8.0
6485	3	0.0	7.3	9.3	8.9	11.2	17.5	20.7	2.6	9.9	3.0	2.0	0.0	29.1
6465	4	9.0	0.0	0.0	1.6	1.4	4.4	1.9	0.0	3.0	3.7	1.2	0.0	11.6
6417	2	0.0	3.1	1.1	4.0	0.0	5.5	0.0	1.0	3.0	3.8	0.0	11.4	19.3
6388	9	2.3	0.0	0.0	9.0	1.4	2.6	0.0	0.0	1.2	0.0	0.0	0.0	13.6
6401	9	1.0	1.7	0.0	0.8	1.4	1.8	0.0	0.0	1.1	0.0	0.0	0.0	13.3
6436	9	5.1	0.0	1.4	0.8	2.3	10.4	0.0	0.0	1.9	0.0	0.0	0.0	13.3
6466	7	4.7	0.0	14.8	10.6	12.9	36.7	41.8	2.8	8.2	4.2	2.2	0.0	10.7
6431	8	7.2	0.0	2.3	3.2	0.0	25.8	1.2	1.9	0.0	0.0	1.7	0.0	70.4
6433	8	5.9	0.0	2.1	3.0	0.0	22.9	F	1.9	4.4	0.0	1.6	0.0	69.2
6450	8	6.5	0.0	2.2	3.8	0.0	26.3	1.2	1.9	4.8	0.0	1.7	0.0	70.1
6402	6	9.0	1.9	0.0	2.0	0.0	6.7	0.0	0.0	2.0	0.0	0.0	0.0	12.4
6516	10	0.0	0.0	2.8	3.6	0.0	20.3	1.7	1.6	4.2	3.4	1.6	0.0	18.5
6527	11	0.0	3.7	2.3	7.4	3.5	9.8	1.3	1.9	5.5	0.0	2.1	0.0	105.5
6500	12	0.0	0.0	0.0	0.0	0.8	4.1	0.0	1.1	2.4	0.0	1.0	0.0	2.8

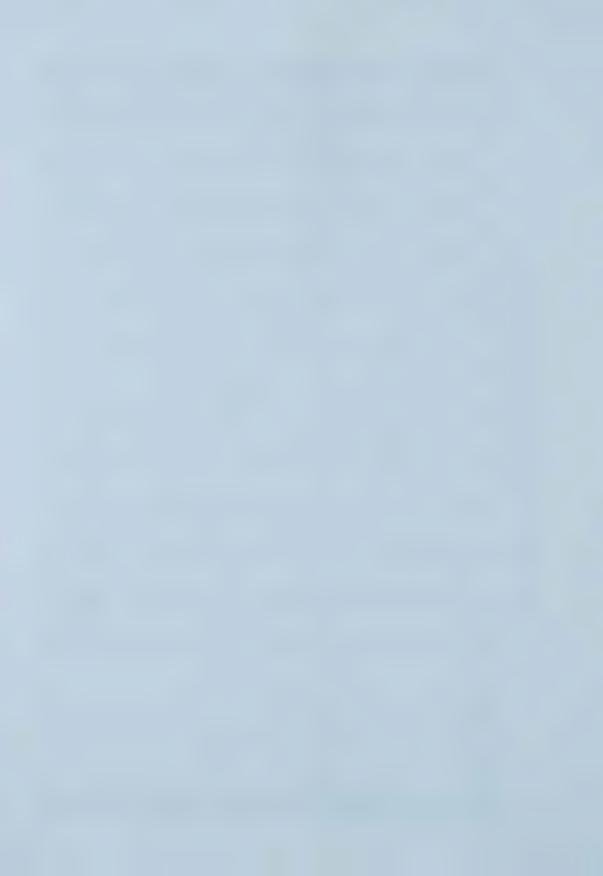


Table A6-2 Fall Sampling Results (continued)

	LIM	12.0	13.3	148.9	75.5	76.7	77.6	22.0	39.1	15.3	66.7	35.9	53.9	19.4	9.4	69.4	26.9	13.0	18.3	34.0	36.5	272.5		0.0	0.0	0.0	0.0
	DEC	0.0	0.0	22.2	10.5	8.9	8.9	0.0	0.0	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	25.6	26.8	121.8		0.0	0.0	0.0	0.0
	×-o	7.9	0.0	8.6	7.3	7.2	7.2	1.1	2.3	2.2	1.3	0.0	2.9	2.0	1.0	2.0	28.5	0.0	1.6	4.0	4.2	9.8		0.0	1.3	0.0	0.0
13)	NON	0.0	0.0	0.0	3.4	3.3	3.2	0.0	0.0	1.5	6.0	0.0	1.2	1.6	0.0	1.8	1.4	0.0	0.0	2.2	2.3	62.6		0.0	0.0	0.0	0.0
m/gm) uo	MPX	21.4	1.9	25.8	0.0	18.7	18.4	2.9	7.8	5.2	3.7	5.2	7.6	5.2	2.6	6.8	84.0	4.0	5.3	8.7	9.5	19.6		1.1	3.5	1.9	1.9
centration	ETH	5.1	0.0	9.4	5.3	5.1	5.1	0.0	2.8	1.5	1.3	1.8	2.3	1.7	0.0	2.3	19.6	1.6	1.8	2.6	2.8	5.9		0.0	1.1	0.0	0.0
rage Cor	OCT	1.9	0.0	8.0	4.6	4.6	4.5	0.0	1.8	6.1	1.9	1.1	4.0	1.4	1.1	2.0	2.8	0.0	1.6	1.7	1.7	17.3	nples	0.0	1.1	0.0	0.0
Time-Weighted Average Concentration (μg/m³)	TOL	17.3	6.1	169.4	28.0	25.3	24.2	3.1	10.6	29.4	14.5	10.4	15.0	11.2	0.9	17.7	43.4	26.9	11.5	48.5	50.1	7.8	Fall Outdoor (96-hour) Samples	2.2	1.6	5.1	6.3
ne-Weigh	HEP	4.4	0.0	0.0	4.9	4.7	4.5	0.0	0.0	0.9	2.7	0.0	0.0	0.0	0.0	0.0	17.0	0.0	0.0	0.0	0.0	10.0	door (96-	0.0	1.8	1.4	0.0
į	BEN	3.5	2.7	25.9	4.7	3.7	3.5	1.3	6.3	2.4	2.3	5.7	3.2	3.7	6.4	6.5	19.7	4.4	6.8	6.4	7.0	5.4	Fall Out	9.0	1.4	1.2	0.0
	MET	4.7	0.0	4.4	4.4	4.2	3.9	0.0	0.0	5.9	6.0	0.0	2.7	0.0	0.0	1.4	17.9	0.0	2.3	0.0	0.0	7.0		0.0	1.5	1.4	6.0
	BUT	0.0	1.6	32.7	5.5	5.5	4.7	0.0	0.0	16.8	3.1	0.0	2.8	4.1	5.1	0.9	0.0	4.4	5.0	8.7	9.8	0.0		0.0	0.0	0.0	0.0
	нех	11.4	0.0	1.3	9.7	8.5	9.6	0.0	0.0	7.0	5.9	0.4	0.2	1.2	0.0	3.3	9.07	10.0	4.6	2.1	2.6	0.0		1.4	0.0	0.0	2.0
	House ID	13	14	15	16	16	16	17	. 18	19	20	21	22	23	24	25	26	27	28	59	29	30		1	2	3	4
	Sampler ID	6456	6508	6526	6461	6534	6550	6408	6510	6384	6459	6389	6492	6390	6424	64.32	6507	6498	6535	6395	6423	6549		6414	6554	6532	6452

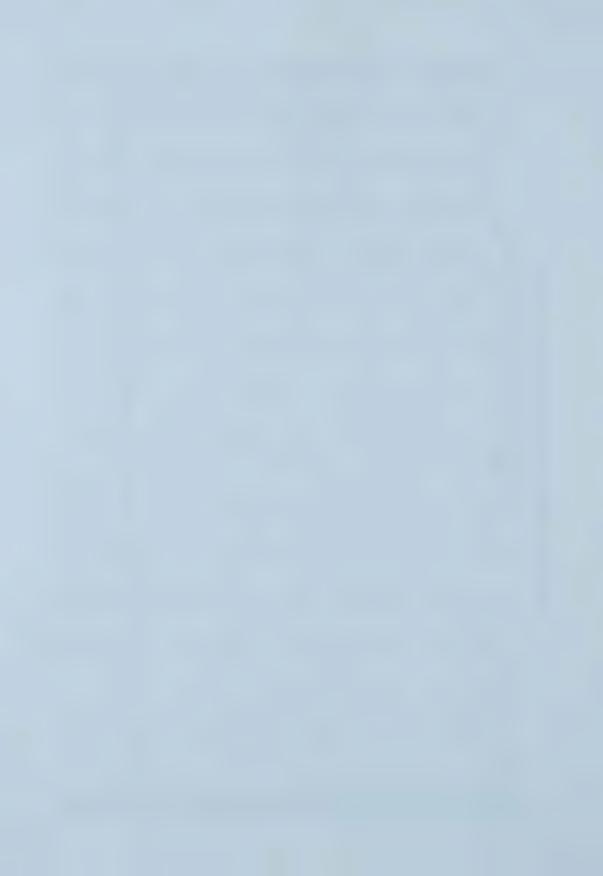


Table A6-2 Fall Sampling Results (continued)

					Ë	Time-Weighted Average	hted Ave		Concentration (µq/m³)	n/pm) no	()			
Sampler ID	House ID	HEX	BUT	MET	BEN	HEP	TOL		ЕТН	MPX	NON	x-0	DEC	LIM
6381	5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
6410	5	0.0	0.0	0.0	9.0	0.0	0.3	0.0	0.0	1.0	0.0	0.0	0.0	0.0
6429	5	0.0	0.0	0.0	0.7	0.0	1.2	0.0	0.0	1.0	0.0	0.0	0.0	0.0
6383	9	0.0	0.0	0.0	0.7	0.0	0.3	0.0	0.0	1.3	0.0	0.0	0.0	0.0
6435	7	0.0	0.0	0.0	1.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6427	8	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6454	6	1.9	0.0	0.0	0.0	0.0	5.9	0.0	0.0	1.3	0.0	0.0	0.0	0.0
6520	10	0.0	0.0	6.0	3.4	1.6	2.8	1.2	0.0	1.8	0.0	0.0	0.0	0.0
6555	7	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0
6497	12	0.0	0.0	6.0	1.0	1.4	4.8	1.0	0.0	1.6	0.0	0.0	0.0	0.0
6439	13	0.0	0.0	0.0	0.0	0.0	4.7	0.0	0.0	1.8	0.0	0.0	0.0	0.0
6512	14	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0
6514	15	0.0	0.0	0.0	3.3	4.9	3.8	4.1	0.0	6.3	0.0	0.0	0.0	0.0
6544	15	0.0	0.0	0.0	0.0	4.5	0.0	0.0	0.0	5.9	0.0	0.0	0.0	0.0
6545	15	0.0	0.0	0.0	0.0	5.5	8.3	4.1	0.0	6.7	0.0	0.0	0.0	0.0
6463	16	0.0	0.0	0.0	2.0	0.0	2.6	0.0	0.0	1.1	0.0	0.0	0.0	0.0
6441	17	1.8	0.0	0.0	6.0	0.0	0.4	0.0	0.0	1.0	0.0	0.0	0.0	0.0
6511	18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0
6387	19	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0
6457	20	2.1	0.0	1.0	0.7	1.6	3.0	1.7	0.5	1.6	6.0	9.0	0.0	0.0
6409	21	0.1	0.0	0.0	0.8	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0
6523	22	0.0	0.0	2.2	1.0	2.2	7.4	1.1	1.0	2.7	0.0	1.1	0.0	0.0
6394	23	6.0	0.0	0.0	0.5	0.0	2.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0
6415	24	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6407	25	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0
6490	26													

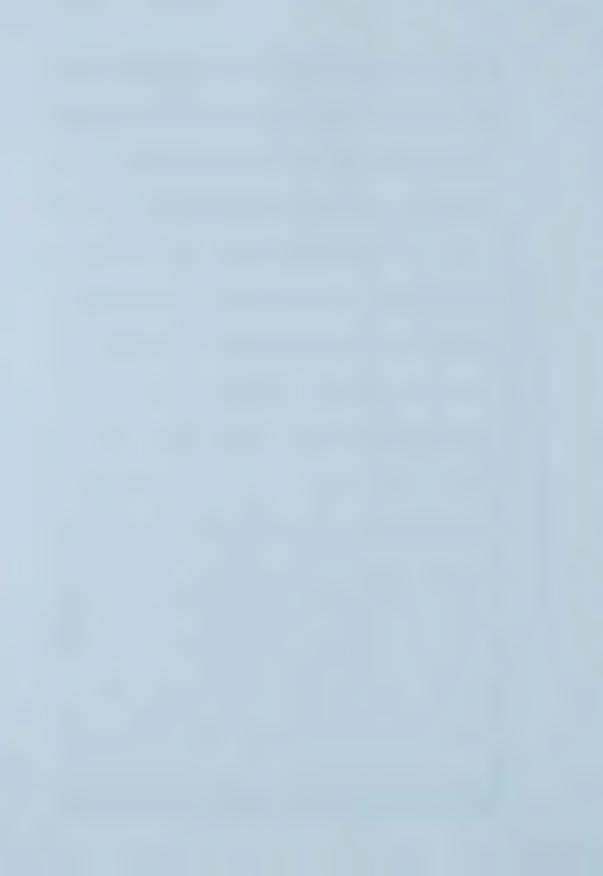


Table A6-2 Fall Sampling Results (continued)

					Tir	Time-Weighted Average Concentration (119/m ³)	ated Ave	rage Co.	ncentrati	מ/טוו) עס	13)			
Sampler ID	House ID	HEX	BUT	MET	BEN	HEP	TOL	OCT	ЕТН	MPX	NON	x-0	DEC	LIM
6504	27	0.8	0.0	0.0	0.8	0.0	0.5	0.0	0.0	1.7	0.0	0.0	0.0	0.0
6543	28	0.0	0.0	1.0	1.0	1.6	0.1	1.0	0.0	1.8	0.0	0.0	0.0	0.0
6425	29	0.2	0.0	0.0	0.8	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6494	30	0.0	0.0	0.0	5.2	4.9	0.7	0.0	0.0	7.9	0.0	0.0	0.0	0.0
					Fall Pers	Fall Personal (24-hour) Samples	-hour) S	amples						
6386	1	9.0	3.6	0.0	0.0	0.0	7.4	0.0	1.2	3.6	0.0	1.2	0.0	19.5
6484	2	11.0	8.8	4.3	8.7	5.4	18.7	0.0	3.8	11.3	0.0	3.8	0.0	10.3
6525	3	0.0	10.8	26.1	13.5	28.0	22.0	51.6	5.1	14.4	7.4	5.1	0.0	38.7
6529	3	0.0	0.0	25.8	13.2	26.9	21.7	50.0	5.1	14.8	7.4	5.1	0.0	35.5
6453	4	0.2	8.8	0.0	5.8	0.0	21.1	0.0	0.0	7.5	5.4	0.0	0.0	17.1
6447	5	7.9	0.0	8.1	16.0	9.9	41.6	0.0	0.0	7.4	4.8	0.0	12.4	8.5
6397	9	4.4	3.6	0.0	6.2	3.5	4.5	0.0	0.0	7.8	0.0	0.0	0.0	15.2
6464	7	1.9	7.8	17.1	12.6	15.3	18.1	33.6	0.0	7.3	0.0	0.0	0.0	38.5
6458	8	11.5	0.0	0.0	3.2	0.0	21.6	0.0	0.0	5.3	0.0	0.0	0.0	60.7
6455	6	9.3	1.4	0.0	2.7	3.8	16.2	0.0	0.0	5.5	0.0	0.0	0.0	50.8
6542	10	0.7	0.0	4.7	9.6	0.0	35.3	0.0	0.0	8.4	4.7	0.0	0.0	34.5
6528	11	0.0	0.0	0.0	15.4	5.8	6.1	0.0	0.0	7.0	0.0	0.0	0.0	154.0
6531	12	21.1	0.0	0.0	5.4	0.0	11.3	0.0	0.0	7.9	0.0	0.0	0.0	31.8
6413	13	13.7	4.1	8.2	8.3	9.7	28.8	0.0	8.1	33.5	0.0	12.2	0.0	20.2
9059	14	0.0	0.0	0.0	3.0	0.0	6.5	0.0	0.0	6.7	0.0	0.0	0.0	7.2
6209	15	5.6	7.9	0.0	7.2	0.0	29.7	0.0	0.0	9.3	0.0	0.0	0.0	31.7
6426	16	6.7	7.3	10.0	6.9	11.1	18.0	16.0	4.7	18.7	5.2	7.0	0.0	43.7
6448	17	20.5	0.0	12.1	13.6	13.2	52.3	10.4	5.9	17.1	0.0	6.2	0.0	40.3
6518	18	0.0	6.5	0.0	13.9	0.0	5.1	0.0	3.9	10.2	0.0	0.0	0.0	74.6
6398	19	15.6	0.0	38.9	3.8	42.7	48.6	94.7	4.8	13.2	14.6	4.4	9.0	15.6
6460	20	3.2	0.0	0.0	15.0	0.0	45.7	0.0	3.9	10.5	0.0	0.0	0.0	20.3

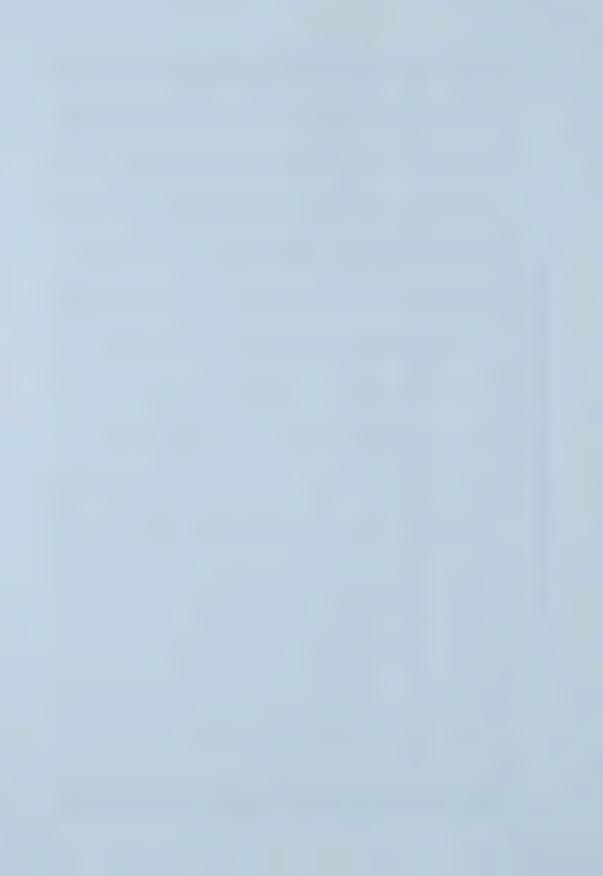


Table A6-2 Fall Sampling Results (continued)

	LIM	9.6	9.09	15.9	7.4	200.0	440	7:4-	23.3	23.3	23.3	23.3 14.3 34.8
	DEC	0.0	5.4	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0 0.0 0.0 29.3
	_	0.0	4.5	0.0	16.6	0.0	17.3		0.0	0.0	0.0	
	×-o		L	L								
ر _ه ر	NON	0.0	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0
u/gπ) uo	MPX	4.9	12.5	10.2	45.5	10.8	50.8	6.1		12.7	12.7	12.7
Time-Weighted Average Concentration (μg/m³)	ЕТН	0.0	3.8	3.8	12.0	0.0	12.8	0.0		3.8	3.8	3.8
rage Col	OCT	0.0	7.0	0.0	4.0	0.0	0.0	0.0		0.0	0.0	0.0
hted Ave	TOL	7.8	32.9	18.5	46.3	21.1	52.0	10.3		46.0	46.0	46.0 17.7 38.8
ne-Weig	HEP	0.0	6.1	0.0	9.5	0.0	12.4	0.0		6.9	6.9	6.9
11	BEN	5.2	5.2	13.8	34.8	12.6	12.5	5.9		8.3	8.3	8.3
	MET	0.0	3.6	0.0	8.4	0.0	14.7	0.0		6.9	9.6	3.6
	BUT	3.1	0.0	11.7	0.0	10.4	0.0	0.0		7.5	7.5	7.5
	HEX	0.0	0.0	4.1	24.6	3.9	30.1	9.1		8.5		
	House ID	21	22	23	24	25	26	27	-	28	28	28
	Sampler ID	6392	6540	6382	6462	6412	6524	6489	0010	6530	6536	6530 6536 6434

3-methylhexane ethylbenzene m,p-xylenes 2-butanone o-xylene benzene heptane toluene decane hexane octane nonane Key HEX BUT MET BEN HEP TOL OCT ETH MPX NON NON O-X

limonene



Table A6-3 Winter Sampling Results



Table A6-3 Winter Sampling Results (continued)

Sampler ID Ho 0063 0060 0061 0044 0004	House ID	HEX	1	MET	REN	NOT THE POOR TOTAL COLUMN	TOI	100	FTH	MDX	NON	×-o	730	Z
0063 0060 0061 0044 0004	22		FO9		בו	ה ה	1)	200		< LIX	252		נו	
0060 0061 0004 0004		0.7	0.0	11.1	7.2	14.0	16.7	19.2	7.8	27.9	4.3	12.9	0.0	45.1
0004 0004 6091	23	0.3	0.0	1.0	1.9	2.0	2.0	1.5	1.0	2.3	1.1	1.2	0.0	3.3
0004	23	0.3	0.0	1.0	1.8	1.9	2.0	1.5	0.0	2.1	0.0	1.1	0.0	3.2
6091	24	3.4	0.0	0.9	8.2	7.9	14.8	0.0	4.4	12.1	0.0	5.5	0.0	43.2
6091	25	15.0	9.1	0.0	11.4	4.8	13.0	0.0	3.9	10.1	0.0	0.0	0.0	8.0
	26	52.7	0.0	15.7	11.9	17.5	62.3	6.2	15.5	61.6	0.0	22.0	0.0	14.5
6103	26	12.0	0.0	8.6	8.5	17.2	12.2	11.3	5.3	14.2	6.7	6.8	0.0	0.0
0053	27	1.2	29.7	0.0	1.2	1.6	4.0	1.4	1.1	3.2	1.8	1.6	0.0	7.1
0024	28	14.0	0.0	12.9	8.2	15.4	17.4	5.9	14.8	60.5	0.0	23.6	4.5	90.5
0100	29	0.0	0.0	0.0	4.9	0.0	13.1	0.0	0.0	6.4	0.0	0.0	8.9	41.0
9800	30	2.0	0.0	0.0	4.3	4.6	0.0	0.0	0.0	6.2	4.2	0.0	0.0	26.7
					Winter Ir	Winter Indoor (96-hour) Samples	-hour) S	amples						
0002	1	2.1	0.0	1.7	3.9	5.0	5.5	2.7	2.0	6.2	1.8	2.7	2.2	23.3
2900	2	11.0	0.0	9.9	4.9	7.8	16.5	3.1	2.6	7.4	1.5	2.7	0.0	11.7
8900	2	21.5	0.0	6.9	5.3	8.1	17.0	3.1	2.4	7.8	1.6	2.9	0.0	12.3
6470	2	11.4	0.0	6.8	6.8	8.0	20.3	3.3	2.9	7.4	1.5	2.9	0.0	11.6
6000	3	2.6	7.4	8.2	12.9	12.1	27.1	18.0	9.7	27.4	3.3	7.3	2.6	125.9
6471	4	10.1	0.0	2.0	4.3	3.9	8.6	2.6	2.4	5.5	1.9	2.1	1.6	16.8
6051	5	1.8	0.0	2.0	4.2	4.2	10.7	1.9	2.0	5.5	1.3	0.0	0.0	30.0
0809	5	4.2	0.0	2.2	4.5	4.4	13.0	2.0	2.0	0.9	1.4	0.0	0.0	30.7
6082	5	6.8	0.0	2.5	6.2	4.9	17.4	2.1	2.2	6.4	1.5	0.0	0.0	30.2
8800	9	1.5	0.0	2.5	2.3	4.5	7.9	3.0	2.0	6.4	2.5	2.7	0.0	12.0
6600	7													
0018	8	2.0	41.4	1.9	3.5	4.9	34.5	2.8	2.8	7.6	1.4	3.2	0.0	8.99
0015	6	2.9	0.0	2.6	2.4	5.3	6.8	4.7	1.6	3.9	1.9	1.7	1.1	16.9
9809	10	4.2	0.0	2.9	11.0	0.9	10.3	5.1	2.3	6.7	1.8	3.3	0.0	35.5



Table A6-3 Winter Sampling Results (continued)

					Ţ	Time-Weighted Average Concentration (ug/m³)	nted Ave	rage Co	ncentrati	on (ua/m	13)			
Sampler ID	House ID	HEX	BUT	MET	BEN	HEP	TOL	OCT	ЕТН	MPX	NON	×-o	DEC	LIM
6042	=	2.7	0.0	1.9	2.8	2.9	6.4	1.8	1.2	2.7	1.2	1.2	1.1	2.6
6087	12	0.8	0.0	1.8	1.8	2.7	5.6	1.8	0.0	2.3	0.0	0.0	0.0	13.8
0040	13	2.2	11.2	5.0	5.3	10.8	24.2	12.7	3.9	10.5	5.5	4.5	1.7	60.2
0025	14	20.2	19.5	3.2	8.3	5.6	80.1	3.8	2.9	9.1	0.9	3.5	32.3	32.8
2800	15	7.9	0.0	6.7	4.0	9.4	21.9	23.0	11.6	45.6	184.6	21.9	439.9	41.9
6483	16	6.6	0.0	4.3	9.5	9.9	23.1	4.8	2.0	13.3	2.2	4.9	3.0	97.5
0054	17	6.5	0.0	4.0	4.3	6.2	20.5	3.9	6.9	23.9	2.2	8.9	2.4	8.3
0057	18	10.0	0.0	2.1	7.3	6.1	14.1	3.1	3.2	9.5	1.6	3.2	0.0	62.0
6024	19	7.7	0.0	4.3	3.5	6.8	19.8	8.4	2.7	8.7	6.5	3.8	8.9	12.6
6035	19	7.3	0.0	4.5	2.2	6.8	19.6	8.3	2.7	8.3	6.2	3.6	8.6	12.3
2000	20	3.8	0.0	3.5	2.8	9.7	11.9	7.9	3.1	10.6	30.3	4.4	35.0	10.0
0085	21	3.8	0.0	4.9	6.1	6.7	27.7	4.1	5.5	18.8	2.5	7.3	0.0	135.0
900	22	3.9	0.0	9.1	6.5	11.8	17.8	17.6	5.0	16.6	3.2	9.9	0.0	64.8
6468	23	3.1	0.0	2.9	5.6	5.5	13.2	3.9	2.6	7.2	1.9	2.8	0.0	14.3
6084	24	4.1	0.0	4.7	5.6	6.2	16.9	3.0	3.1	10.3	0.0	4.0	0.0	39.1
6475	24	4.9	0.0	4.5	5.3	6.1	19.5	3.2	3.2	10.3	2.1	4.0	1.3	39.1
0003	25	3.5	6.9	3.1	7.8	5.1	14.8	2.6	2.7	8.7	2.2	3.0	0.0	7.4
6062	56	59.3	0.0	17.5	11.4	16.4	44.4	4.1	16.5	71.0	2.4	24.0	2.6	21.8
6479	27	12.4	105.3	2.6	4.0	4.9	29.1	4.6	4.4	14.2	9.7	0.9	8.4	12.4
0026	28	11.9	0.0	6.2	6.5	9.4	15.0	2.9	6.5	25.8	2.2	10.1	0.0	38.1
9600	29	22.1	0.0	2.0	8.2	0.0	22.1	2.5	5.6	7.3	0.0	3.1	6.7	41.1
0105	29	18.5	0.0	2.0	8.2	0.0	22.2	2.3	5.6	9.7	0.0	3.1	6.9	40.1
6041	30	6.1	0.0	2.5	3.8	4.6	11.3	3.0	2.3	7.4	4.1	3.3	8.2	83.3
					Vinter Or	Winter Outdoor (96-hour) Samples	8-hour)	Samples						
6032	1	2.7	0.0	1.6	3.8	3.6	3.7	2.5	1.1	2.2	1.5	1.1	0.0	0.0
6478	2	2.3	0.0	2.4	4.6	4.2	6.2	3.3	1.8	5.0	1.6	2.1	0.0	0.0

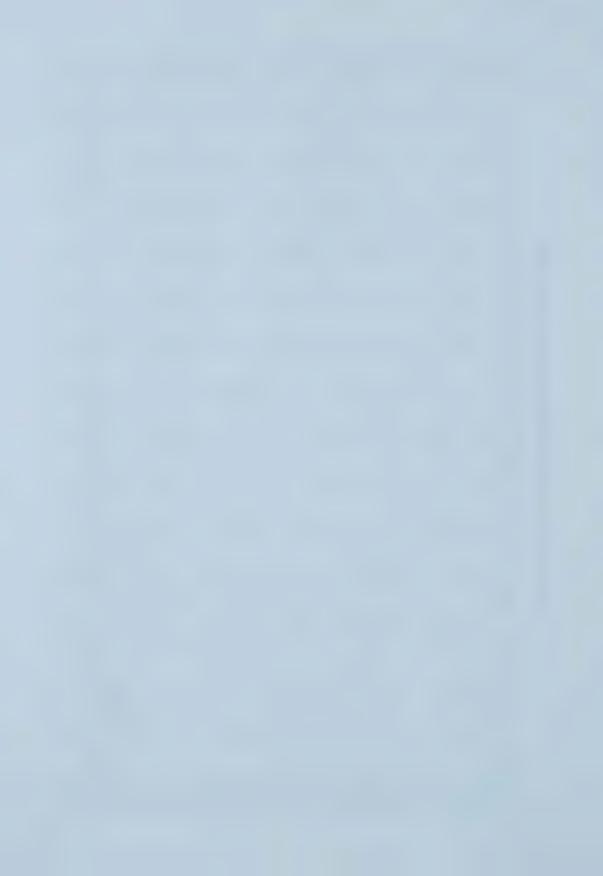


Table A6-3 Winter Sampling Results (continued)

					Ē	Time-Weighted Average Concentration (µg/m³)	nted Ave	rage Co	ncentrati	on (µg/n	13)			
Sampler ID	House ID	НЕХ	BUT	MET	BEN	HEP	TOL	OCT	ЕТН	MPX	NON	x-o	DEC	LIM
6031	3	1.3	0.0	1.5	1.8	3.0	3.2	2.2	1.1	3.2	1.4	0.0	0.0	0.0
0045	4	1.6	0.0	2.4	2.4	4.1	3.2	3.2	1.7	5.1	1.6	2.1	0.0	0.0
0020	4	6.0	0.0	2.4	2.4	4.2	3.6	3.1	2.0	5.1	1.6	2.1	0.0	1.1
0074	4	7.1	0.0	2.4	2.4	4.2	4.3	3.1	1.8	5.1	1.6	2.2	0.0	6.0
0034	5	0.9	0.0	1.2	1.8	2.4	1.6	1.4	0.0	2.7	0.0	0.0	0.0	0.0
6800	9	1.1	0.0	2.0	1.9	3.6	2.9	2.9	1.5	4.5	1.5	2.2	0.0	0.0
0102	7													
9609	8	3.2	0.0	2.9	4.2	5.0	7.5	3.2	1.9	5.0	1.8	2.0	0.0	0.0
0013	6	2.4	0.0	2.2	1.9	4.3	3.6	3.0	1.3	3.8	1.6	1.8	0.0	6.0
8000	10	2.3	0.0	1.3	1.5	3.2	1.6	2.2	1.0	2.1	1.3	1.0	0.0	0.0
2000	11	1.6	0.0	1.7	1.6	3.5	2.9	2.5	1.0	2.4	1.4	1.1	0.0	0.0
0030	12	0.0	0.0	6.0	1.6	2.2	2.6	2.1	0.0	1.5	0.0	0.0	0.0	0.0
0042	13	0.4	0.0	1.2	1.3	3.1	0.3	2.5	0.0	1.6	1.2	0.0	0.0	0.0
0022	14	0.3	0.0	1.1	1.5	2.4	1.1	0.0	0.0	2.0	1.1	0.0	0.0	0.0
0029	15	0.8	0.0	1.7	1.7	3.5	2.7	2.5	1.2	2.7	0.0	0.0	0.0	0.7
0043	16	4.1	0.0	1.7	2.3	2.7	2.6	1.9	0.0	3.8	1.1	1.5	0.0	0.0
0020	17	1.7	0.0	2.2	2.5	4.0	4.0	3.2	1.4	4.4	1.6	1.9	0.0	1.1
0058	18	2.7	0.0	2.0	2.2	3.7	4.2	3.0	1.3	3.9	1.4	1.8	0.0	1.0
6013	19	11.2	0.0	3.7	2.9	3.9	10.1	1.3	3.7	15.2	0.0	5.6	0.0	3.9
6033	20	3.7	0.0	2.4	2.2	4.7	2.0	2.8	1.5	4.2	1.8	1.8	0.0	0.0
6052	20	4.4	0.0	2.8	2.5	5.4	7.3	3.3	1.8	4.9	2.0	2.1	0.0	0.0
0075	21	2.3	0.0	3.5	2.9	4.9	8.2	3.4	2.6	7.9	1.7	3.4	0.0	0.0
9900	22	2.5	0.0	3.8	2.9	5.3	10.3	3.4	2.8	8.8	2.3	3.6	0.0	0.8
6482	23	1.4	0.0	2.4	2.5	4.1	10.1	2.9	2.1	5.9	1.8	2.3	0.0	0.0
0041	24	4.2	0.0	7.1	3.9	7.7	17.8	3.7	4.1	14.6	2.1	5.6	0.0	9.0
6026	25	1.4	0.0	1.5	2.0	2.8	3.3	2.0	1.1	3.0	1.2	1.2	0.0	0.0

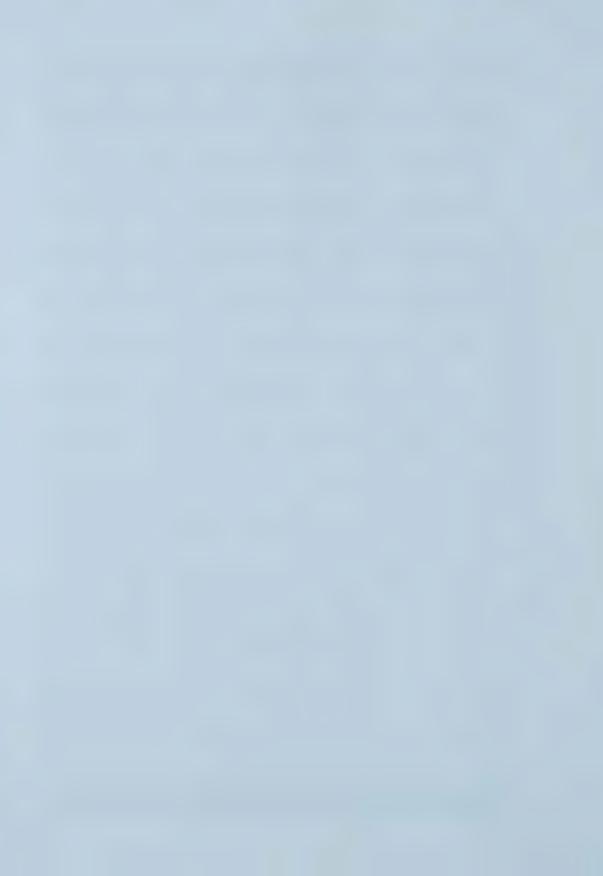


Table A6-3 Winter Sampling Results (continued)

ן פו ספווסח	AEV.	Tila	TAK	NEG	7 015	Į.	700	בדם	LED TO OCT ETH MDV		>	0	1 184
2	HEX 10	10	ME L	BEN 17	HEP 3.1	10L	100	H .	MPX	NON	×-o	DEC	LIM
27	0.00	0.0	. 6	2.6	3.6	2.6	2.8	0.0	4.1	0.0	1.6	0.0	0.0
28	2.3	0.0	1.8	2.4	3.2	5.9	1.6	1.3	4.3	1.2	0.0	0.0	0.0
28	5.4	0.0	1.6	2.4	2.8	4.0	1.4	1.2	4.3	1.1	0.0	0.0	0.0
28	2.5	0.0	1.7	2.4	3.0	4.7	1.6	1.2	4.2	1.1	0.0	0.0	0.0
29	0.0	0.0	0.0	2.7	2.8	0.5	1.8	0.0	2.6	0.0	0.0	0.0	0.0
29	6.1	0.0	1.6	2.8	3.0	1.1	2.0	0.0	2.6	0.0	0.0	0.0	0.0
30	2.2	0.0	2.4	2.3	3.6	4.2	2.2	1.7	4.9	1.5	2.2	0.0	0.0
				Vinter Pe	Winter Personal (24-hour)		Samples						
_	3.6	0.0	0.0	7.0	7.9	8.0	0.0	0.0	8.9	0.0	4.6	0.0	39.1
_	2.6	0.0	0.0	7.3	7.5	12.3	4.3	3.8	7.8	0.0	3.8	0.0	36.7
2	10.7	8.0	17.2	5.0	16.8	0.9	0.0	0.0	7.0	0.0	3.8	0.0	9.7
က	0.1	12.8	30.7	19.7	30.3	62.2	63.9	9.1	26.4	8.8	7.6	0.0	108.4
4	0.0	12.1	0.0	5.3	0.0	4.0	0.0	0.0	7.5	0.0	3.8	0.0	20.2
4	2.6	10.9	5.0	10.0	5.4	19.0	0.0	0.0	7.4	0.0	3.8	0.0	17.4
5	4.7	0.0	3.7	5.7	7.4	36.5	0.0	0.0	7.0	0.0	0.0	0.0	25.4
9	2.2	0.0	5.2	7.7	5.9	9.0	3.8	4.8	15.3	0.0	7.0	0.0	10.4
7	19.7	0.0	0.0	8.2	7.5	19.4	0.0	0.0	12.1	0.0	5.6	0.0	21.6
8	15.9	44.7	0.0	4.2	0.0	50.5	0.0	0.0	12.2	0.0	5.1	0.0	6.97
6	10.9	0.0	0.0	3.3	3.8	5.2	5.2	0.0	4.4	0.0	0.0	0.0	16.0
10	2.4	0.0	6.5	16.7	7.7	15.7	11.5	5.0	11.6	0.0	4.7	0.0	29.1
11	23.2	0.0	5.0	10.9	7.2	34.7	4.3	6.9	22.9	5.9	8.0	9.5	12.7
12	3.8	0.0	0.0	0.0	4.1	4.6	0.0	0.0	5.1	0.0	0.0	0.0	18.4
13	1.4	0.0	5.3	5.2	12.0	12.8	9.8	0.0	8.9	5.3	4.4	0.0	13.7
14	3.7	21.3	0.0	27.7	6.1	88.8	0.0	4.7	11.1	6.7	0.0	25.3	26.7
15	5.7	0	150	C	V 0 T	007	0	7 7 0	O F O	0 777	0 , ,	0000	1



Table A6-3 Winter Sampling Results (continued)

Sampler ID	House ID	HEX	BUT	MET	Tir	Time-Weighted Average Concentration (μg/m³)	hted Ave	oct OCT	ncentrati	on (µg/m	(EL	×-o	DEC	Z.
	15	7.0	0.0	22.0	9.5	26.0	45.9	71.7	23.3	89.4	434.9	45.0	924.0	65.3
	16	11.6	0.0	5.2	12.7	9.3	17.8	8.5	7.1	20.5	4.8	8.3	9.8	50.9
	16	5.2	0.0	6.3	11.8	10.1	38.4	8.5	7.5	21.3	5.2	8.3	0.0	40.2
	17	4.3	0.0	6.7	7.9	11.2	30.2	5.1	9.5	34.1	0.0	14.1	0.0	17.7
	18	0.0	0.0	0.0	7.4	5.6	11.3	0.0	0.0	9.8	0.0	4.8	0.0	38.0
	19	15.5	0.0	9.8	7.4	11.5	42.9	9.5	0.0	15.2	4.9	5.6	0.0	24.1
	20	11.4	0.0	19.8	18.7	24.0	66.4	10.6	12.2	40.1	4.9	12.1	0.0	13.2
0078	21	0.0	0.0	4.7	5.9	5.8	13.7	0.0	5.0	14.7	0.0	6.1	0.0	9.4
	22	0.0	0.0	38.2	8.4	35.3	13.9	78.7	8.9	31.7	8.2	14.4	0.0	52.1
	23	1.7	0.0	1.3	3.4	2.4	6.2	1.8	1.3	2.7	1.2	1.2	0.0	4.3
9000	24	1.7	0.0	5.5	13.5	7.0	36.8	0.0	5.1	15.2	0.0	0.0	0.0	8.3
	25	27.5	0.0	9.0	8.7	10.7	28.1	5.1	10.2	38.9	0.0	13.7	0.0	13.1
0055	26	0.3	28.0	0.0	1.2	1.7	4.0	1.9	1.1	3.2	1.8	1.7	0.0	6.7
	27	35.7	0.0	14.7	12.6	18.7	38.8	9.9	16.7	67.6	0.0	26.2	0.0	111.5
	28	0.2	0.0	0.0	4.6	4.3	12.1	0.0	0.0	0.9	0.0	0.0	5.8	24.3
	29	6.2	0.0	5.7	4.9	7.5	15.1	3.9	0.0	7.7	4.2	3.8	0.0	23.7
	hexane			ETH		ethylbenzene	zene							
	2-butanone	a)		MPX		m, p-xylenes	enes							
	3-methylhexan	exane		NON		nonane								
	benzene			X-0		o-xylenes	S							
	heptane			DEC		decane								

limonene

M

toluene

TOL OCT



Appendix 7: Notes on Statistical Methods

A7.1	Intraclass Correlation Coefficients	190
A7.2	Shapiro-Wilk W Test for Normality	191



A7.1 Intraclass Correlation Coefficients

The intraclass correlation coefficients (ICC) were calculated using a Microsoft Excel spreadsheet based on the following equations (Haggard, 1958; Box et al, 1978):

$$ICC = \frac{BMS - WMS}{BMS + (1 - k')WMS},$$
 (Eqn. A7-1)

$$BMS = \sum_{t=1}^{n} \frac{k_t (\overline{y}_t - \overline{y})^2}{n-1},$$
 (Eqn. A7-2)

WMS =
$$\sum_{t=1}^{n} \sum_{i=1}^{k_t} \frac{(y_{ti} - \overline{y}_t)^2}{N - n}$$
, and (Eqn. A7-3)

$$k' = \frac{1}{n-1} \left(\sum_{t=1}^{n} k_t - \frac{\sum_{t=1}^{n} k_t^2}{\sum_{t=1}^{n} k_t} \right);$$
 (Eqn. A7-4)

where

n is the number of sampling locations;

N is the total number of observations;

 k_t is the number of observations (replicates) at the t^{th} sampling location; and y_{ti} is the i^{th} observation at the t^{th} sampling location.

References

Box, G. E. P., W. G. Hunter, and J. S. Hunter. 1978. <u>Statistics for Experimenters</u>. New York, NY: John Wiley & Sons.

Haggard, E. A. 1958. <u>Intraclass Correlation and the Analysis of Variance</u>. New York, NY: Dryden Press.

Koch, G. G. 1983. Intraclass correlation coefficient. In: S. Kotz and N. L. Johnson (eds.) Encyclopedia of Statistical Sciences, Vol. 4: 212-217. New York, NY: John Wiley & Sons.



A7.2 Shapiro-Wilk W Test for Normality

The Shapiro-Wilk W test was applied to log-transformed data using a C program based on the AS R94 algorithm (Royston, 1995). The algorithm takes as its arguments a vector of observations sorted in ascending order, the uncensored sample size, and the number of censored values. While the algorithm expects right (upper-tail) censoring, data with left (lower-tail) censoring can be processed by changing the sign of all observations. The algorithm approximates the W statistic and associated tabulated probability given by the equation (Shapiro and Wilk, 1965):

$$W = \frac{\left(\sum_{i=1}^{n} a_{i} x_{i}\right)^{2}}{\sum_{i=1}^{n} (x_{i} - \overline{x})^{2}},$$
 (Eqn. A7-5)

where:

 $x = \{x_1, x_2, x_3, ..., x_n\}$ is a vector of observations in ascending order; and $a = \{a_1, a_2, a_3, ..., a_n\}$ is a vector of coefficients tabulated by Shapiro and Wilk (1965).

References

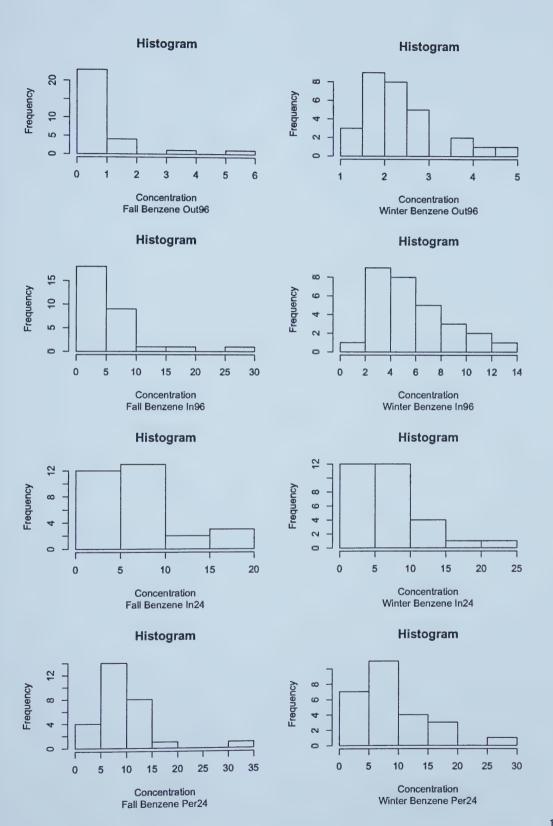
- Royston, P. 1993. A toolkit for testing for non-normality in complete and censored samples. <u>Statistician</u> 42: 37-43.
- Royston, P. 1995. Remark AS R94: a remark on algorithm AS 181: the \$W\$-test for normality. <u>Applied Statistics</u> 44:547-551.
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- Shapiro, S. S., M. B. Wilk, and H. J. Chen. 1968. A comparative study of various tests for normality. <u>Journal of the American Statistical Association</u> 63: 1343-1372.



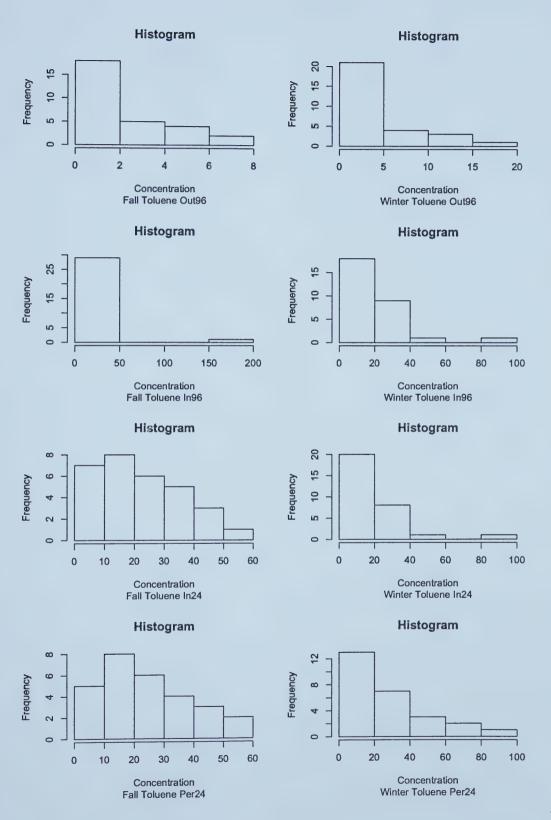
Appendix 8: Histograms and Probability Plots

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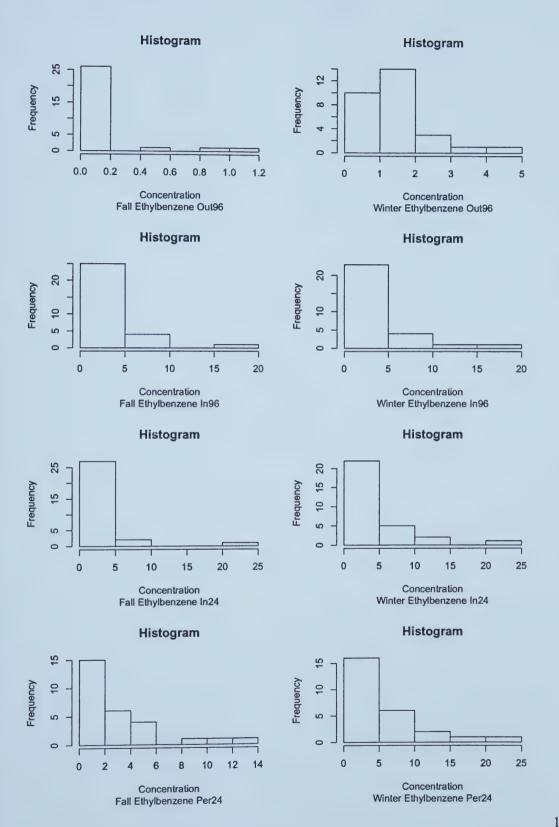


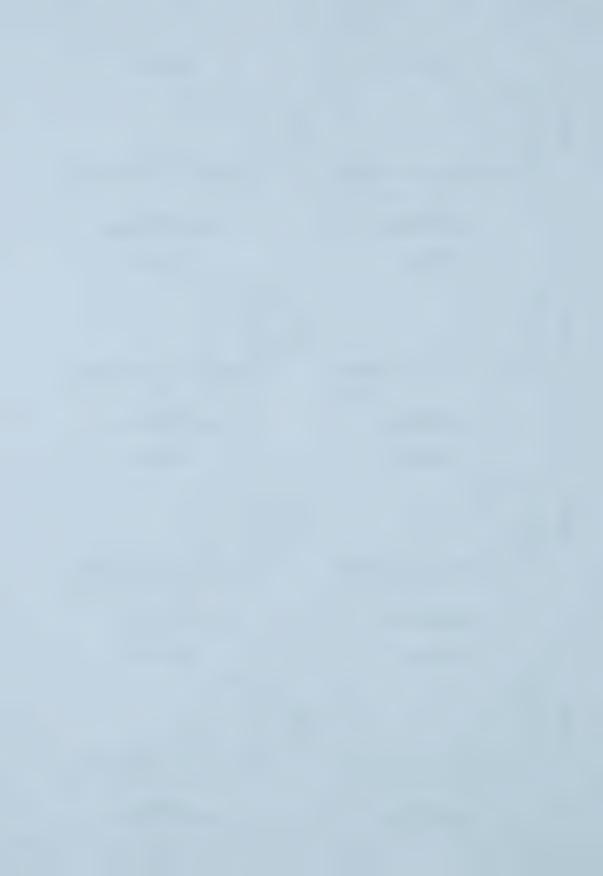


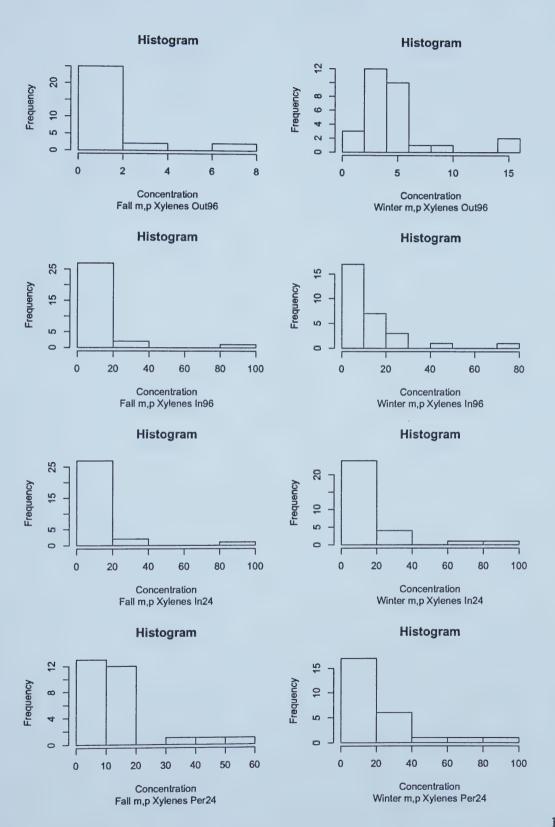




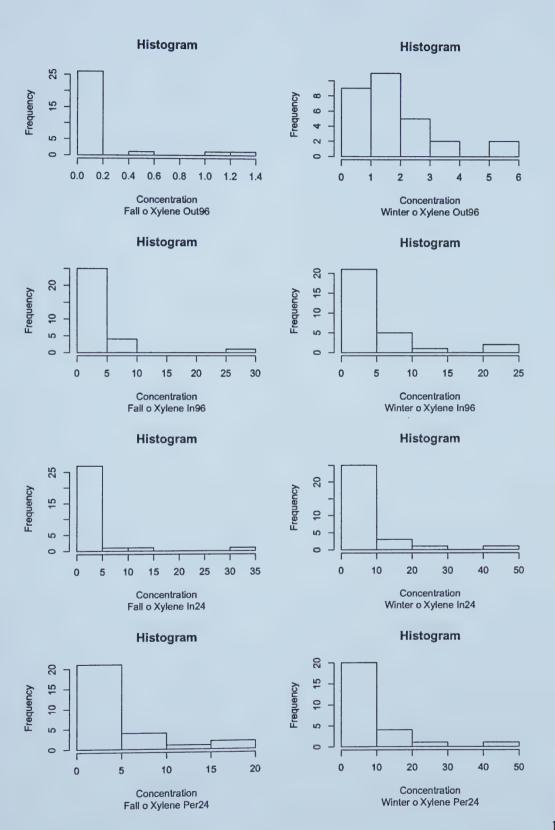




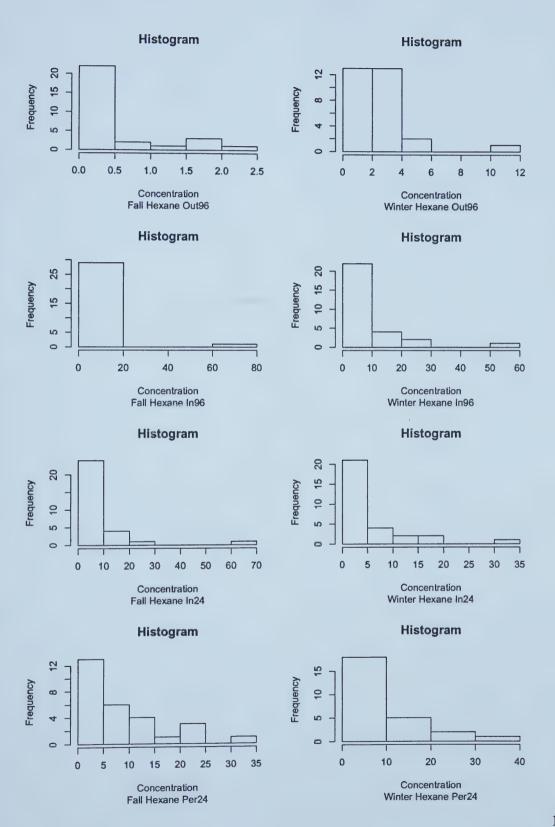




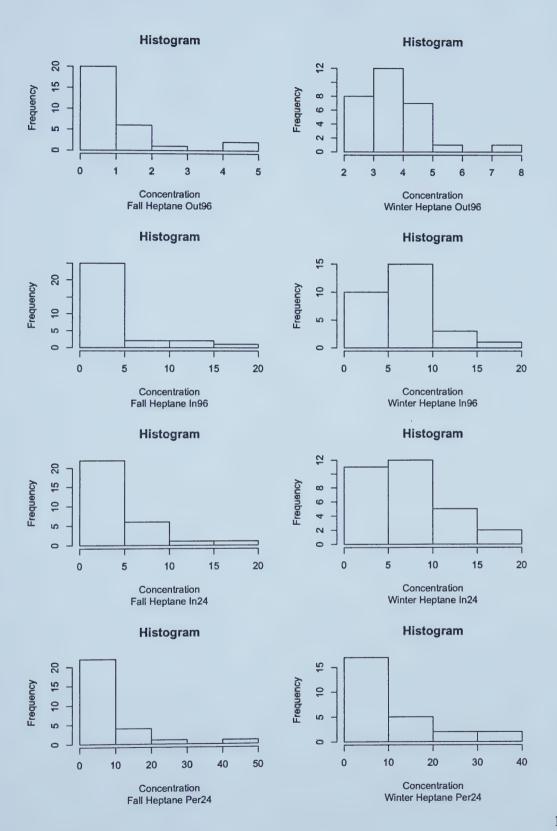




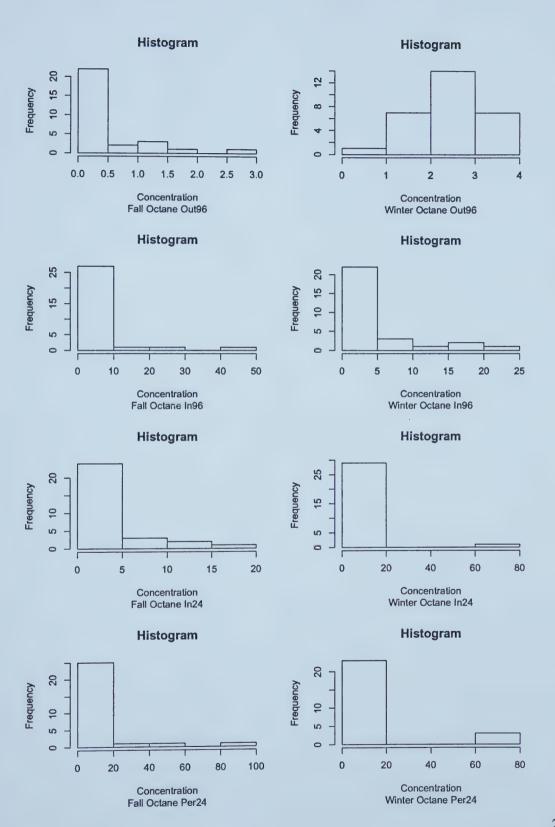




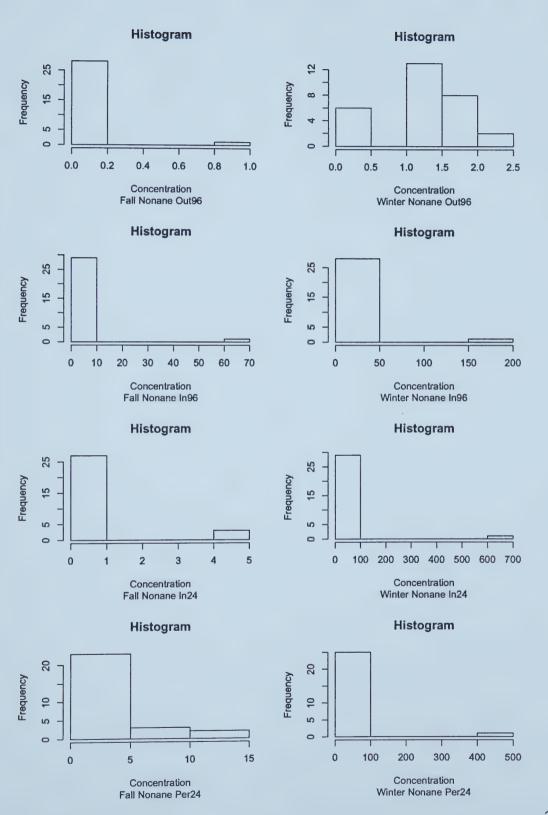


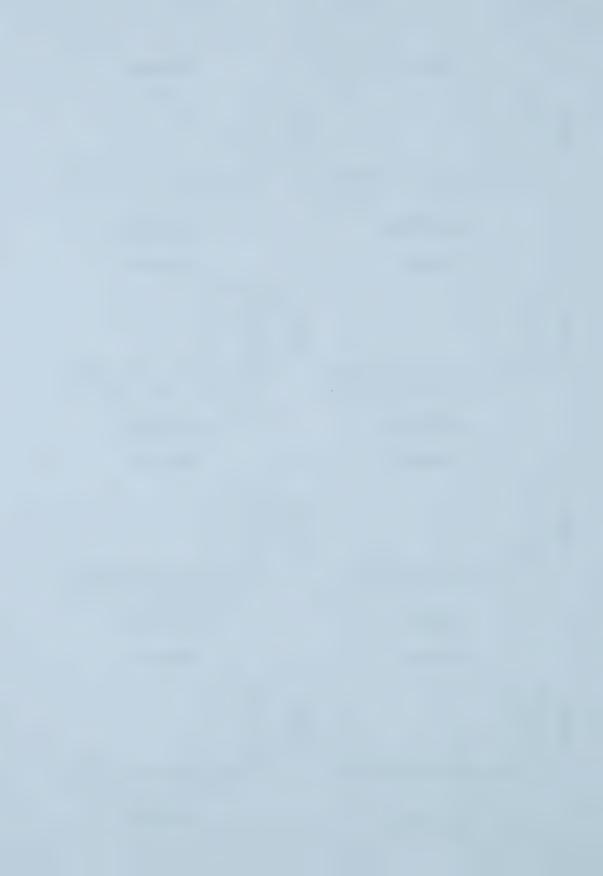


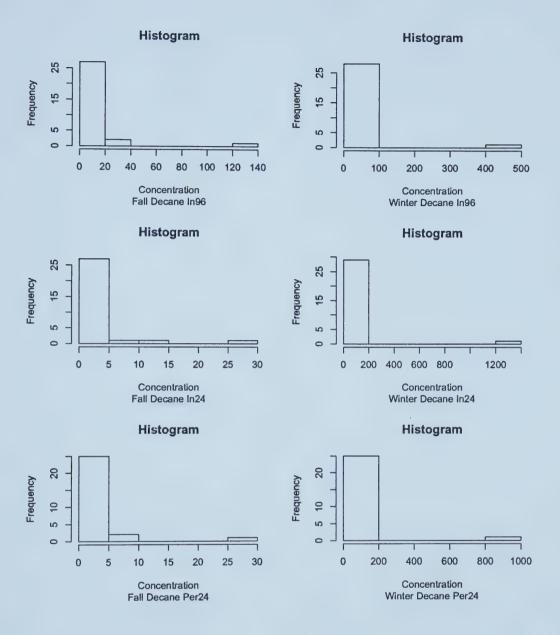




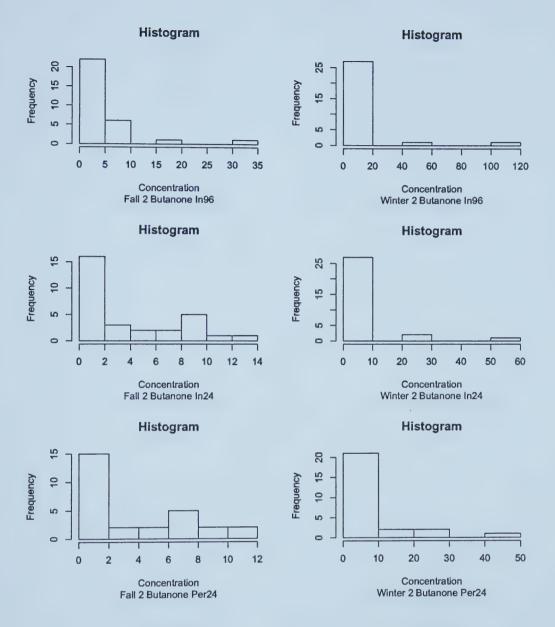




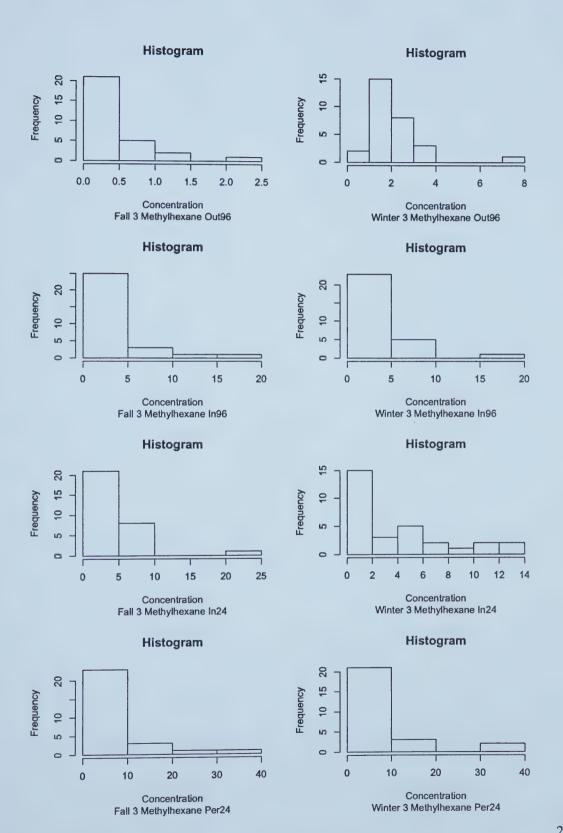




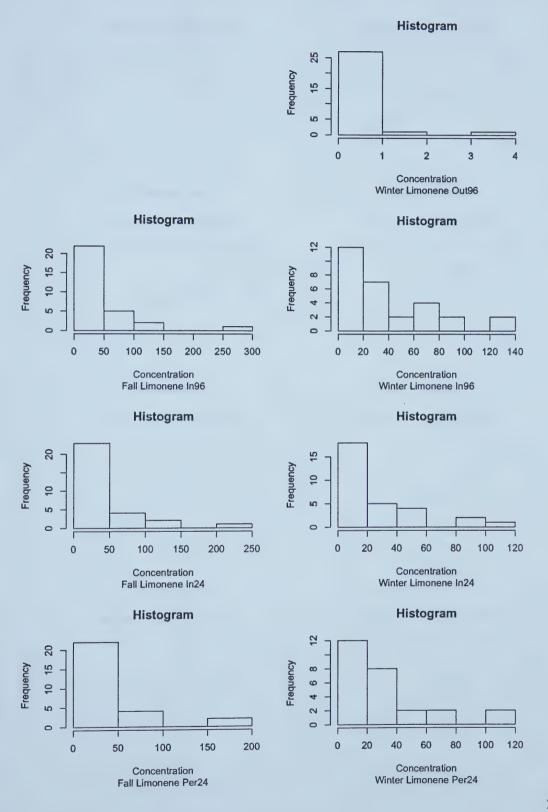




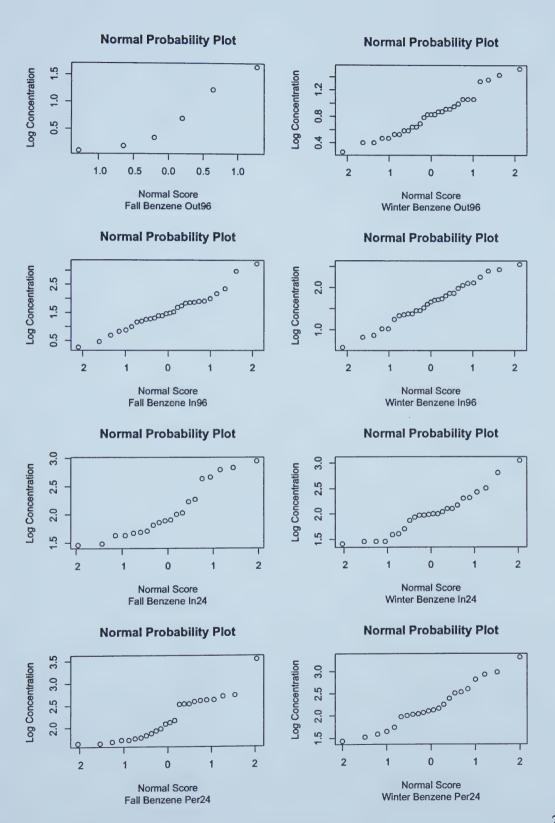


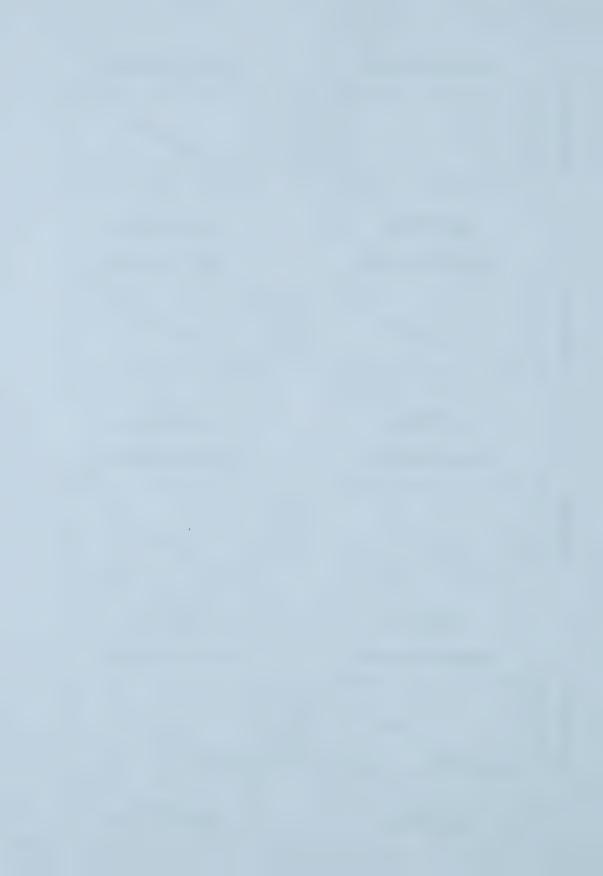


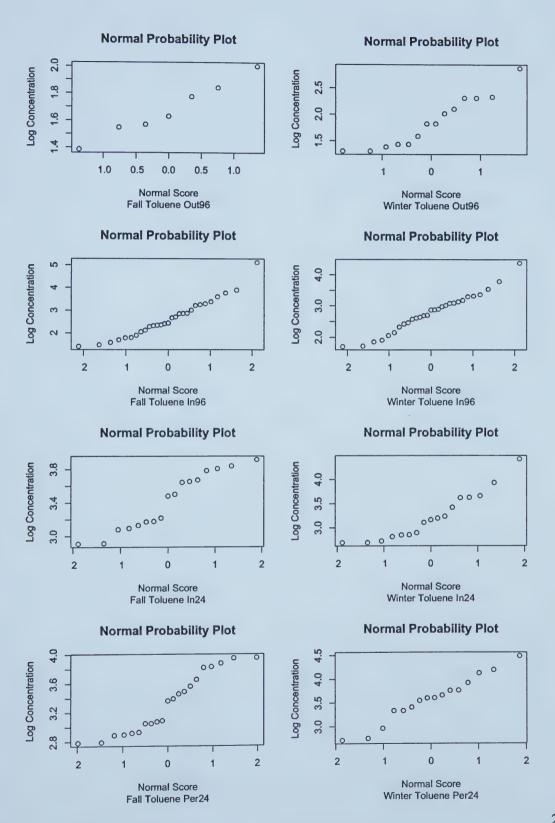




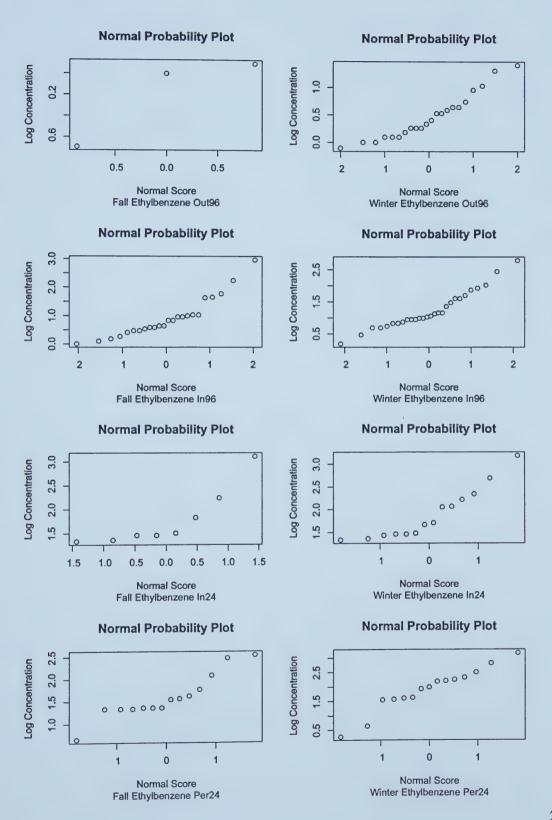




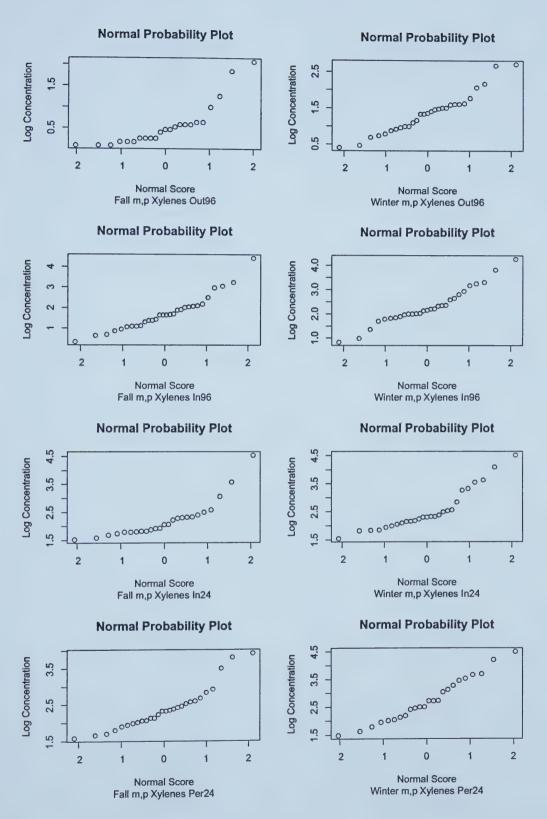




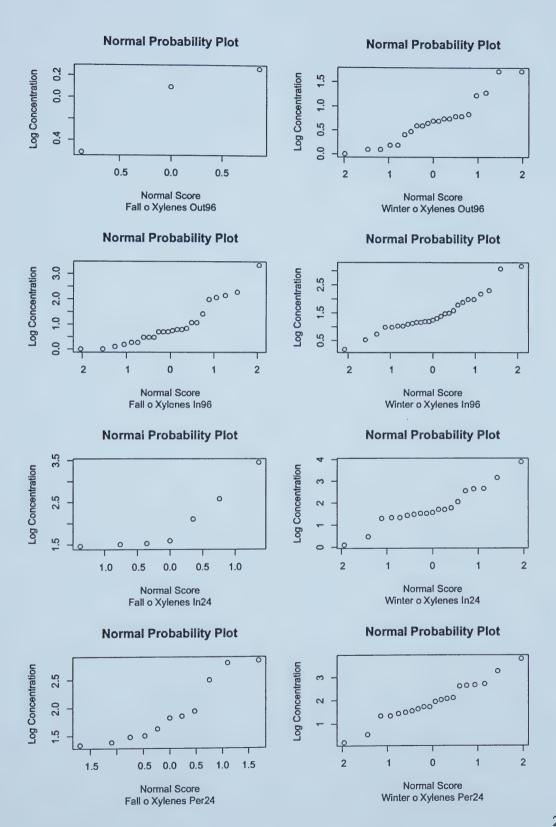




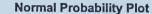


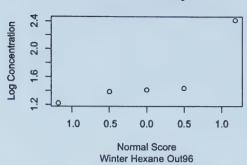




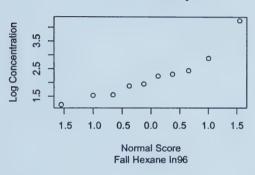




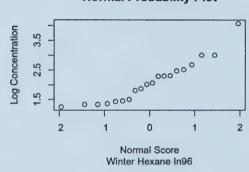




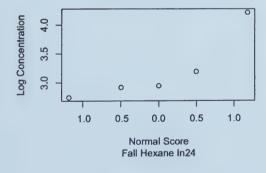
Normal Probability Plot



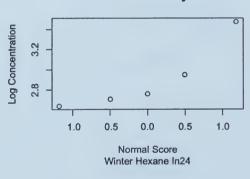
Normal Probability Plot



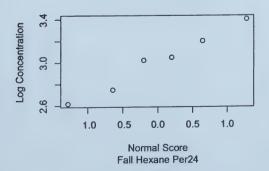
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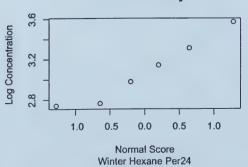
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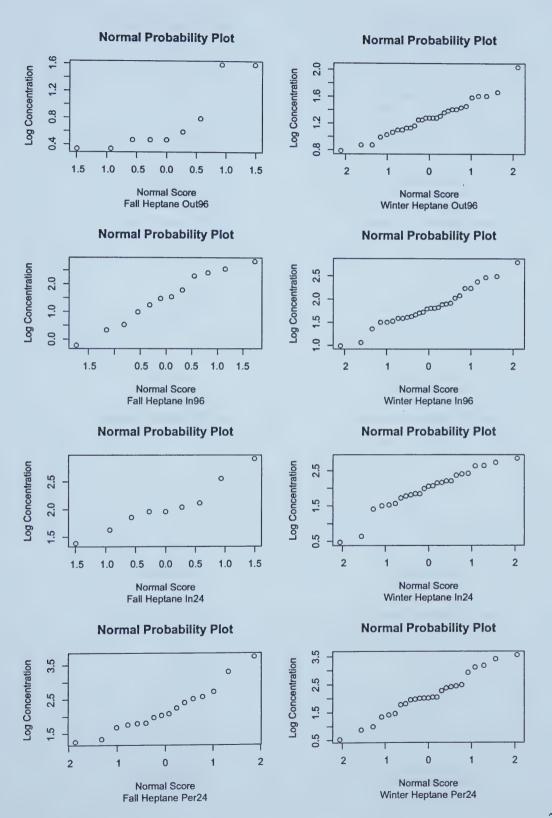
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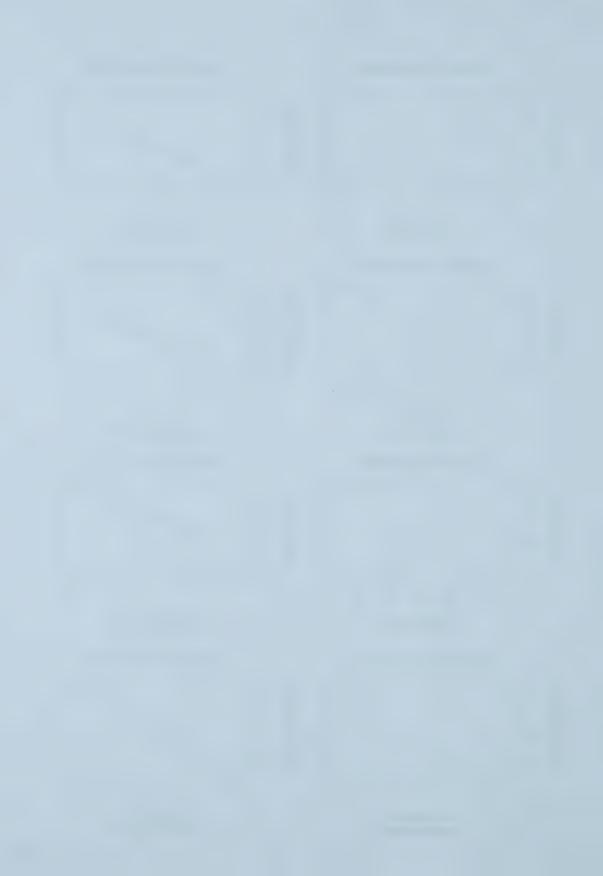


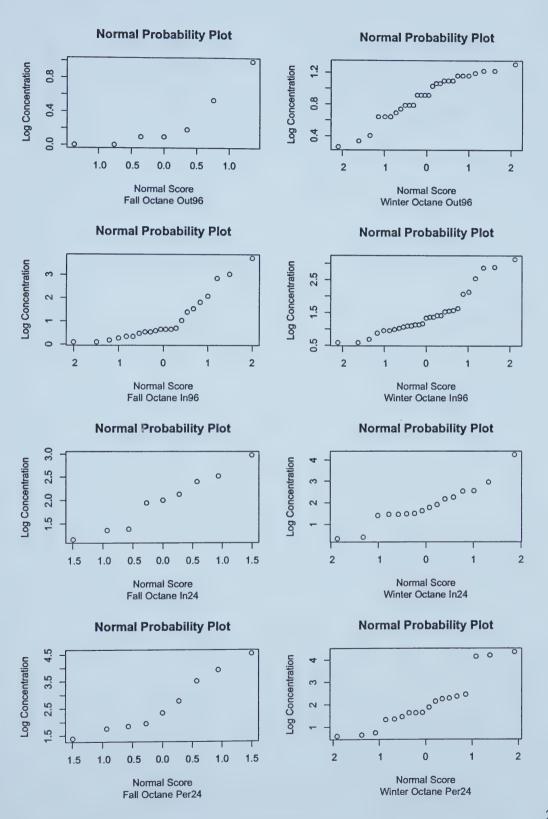
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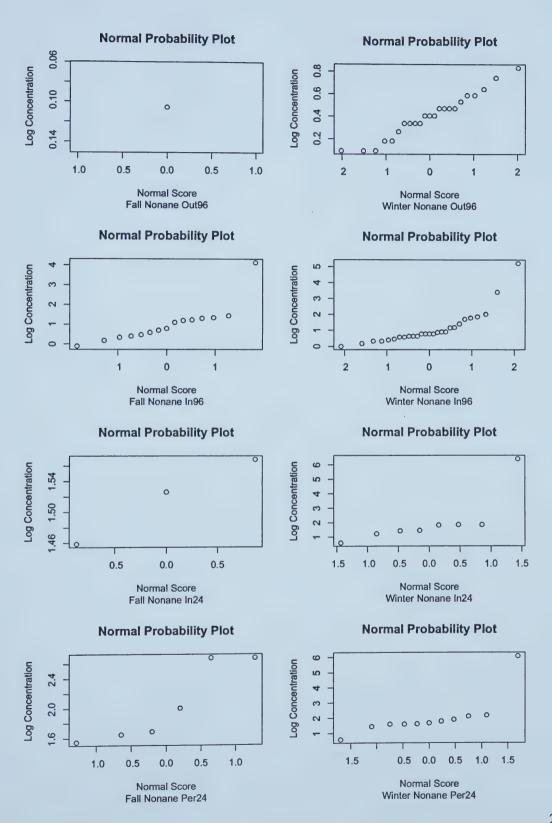


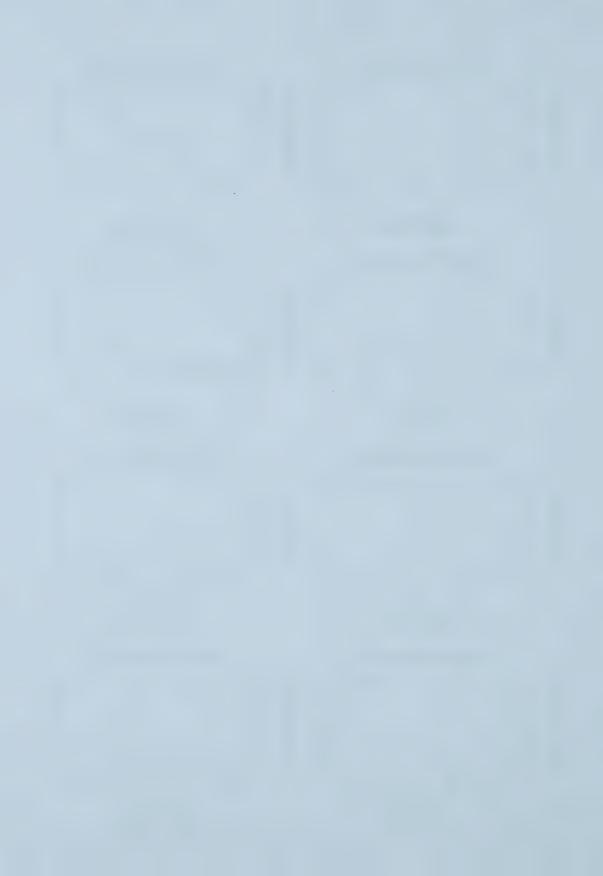


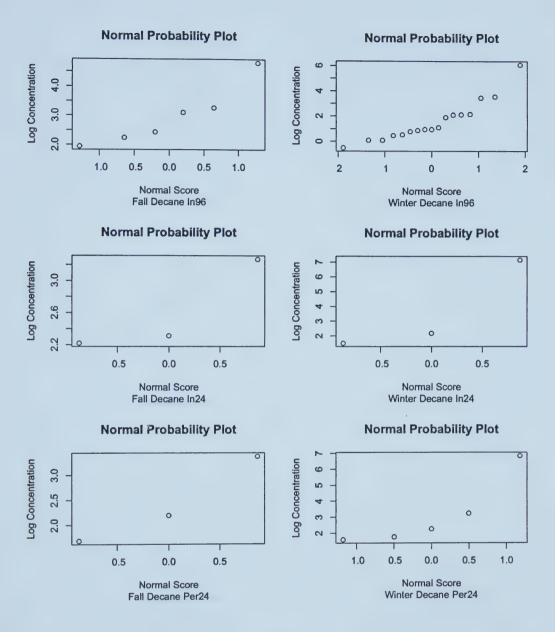




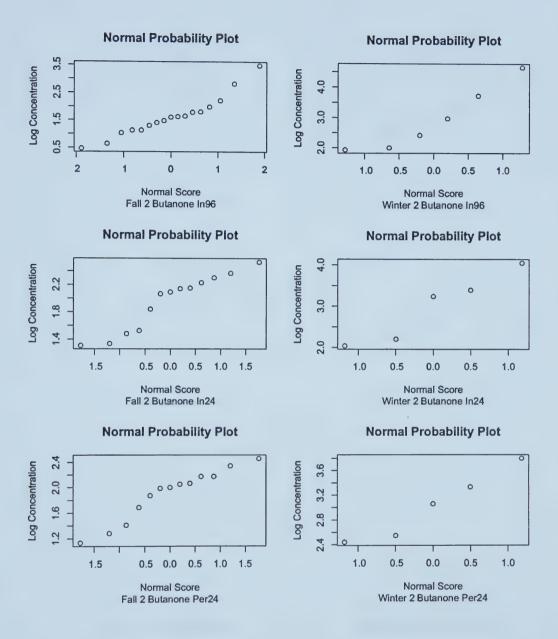




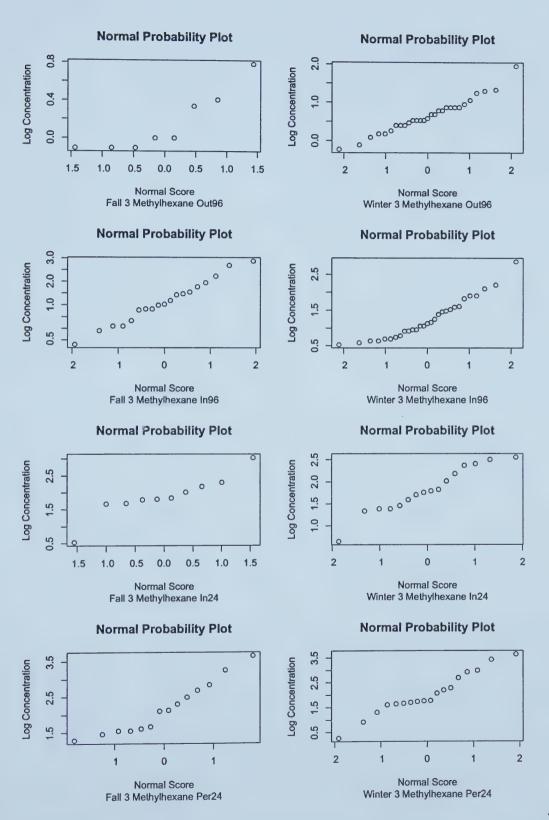




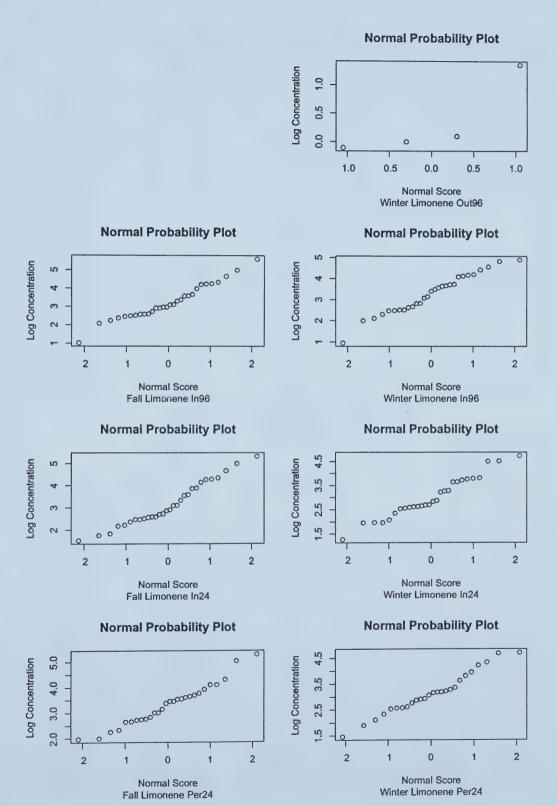












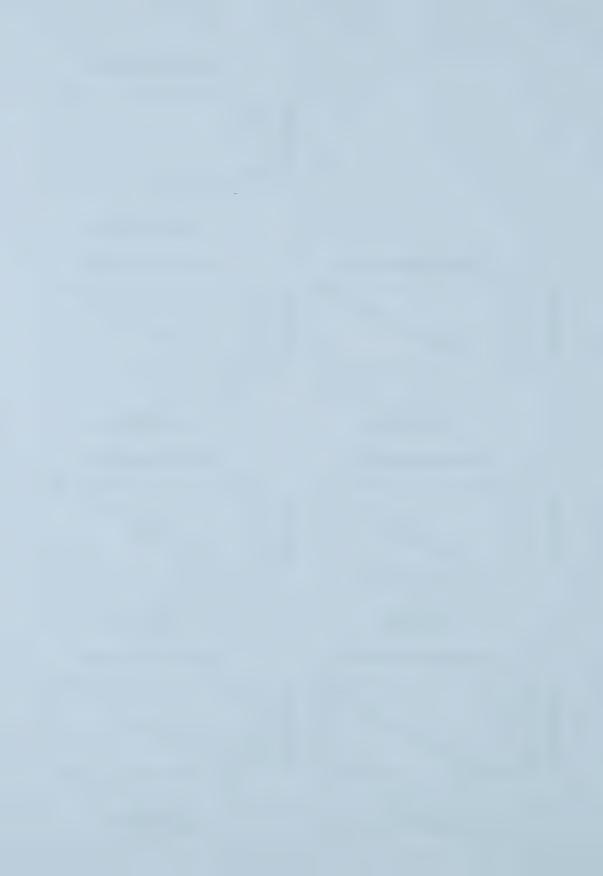
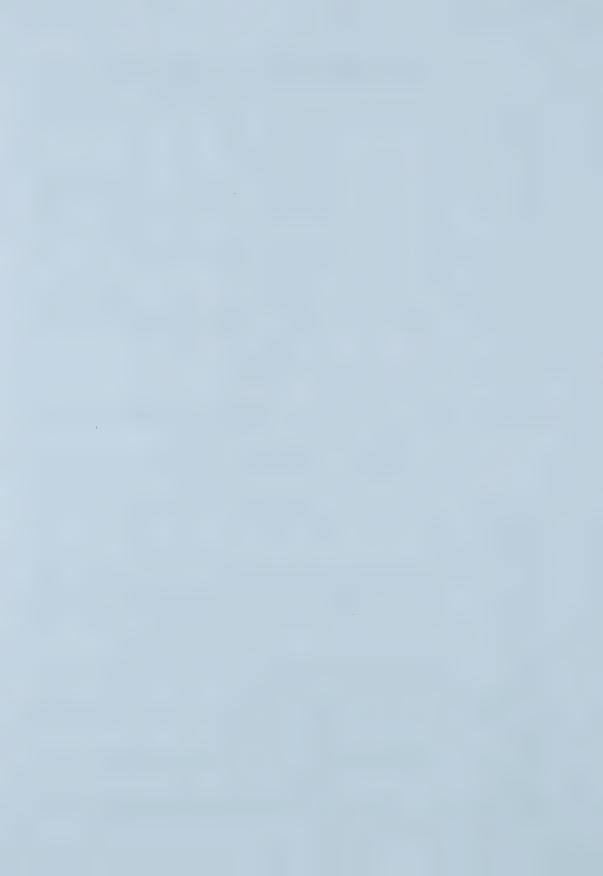


Table A8-1 Fall Shapiro-Wilk Results

	Outdoor 96		Indoor 96		Indoor 24		Personal 24	
	W	P	W	P	W	P	W	P
Hexane								
2-Butanone			0.9638	0.8113				
3-Methylhexane			0.9370	0.3001			0.9762	0.9844
Benzene			0.9704	0.5821	0.9419	0.3191	0.9367	0.1366
Heptane							0.9814	0.9915
Toluene			0.9733	0.6431	0.8739	0.0427		
Octane			0.9254	0.1129				
Ethylbenzene			0.9481	0.2572			0.8840	0.1209
m,p-Xylenes	0.8901	0.0207	0.9280	0.0433	0.8679	0.0037	0.8926	0.0077
Nonane			0.8505	0.0352				
o-Xylene			0.9464	0.2363				
Decane								
Limonene			0.9679	0.4839	0.9564	0.2492	0.9668	0.4967

Table A8-2 Winter Shapiro-Wilk Results

	Outdoor 96		Indoor 96		Indoor 24		Personal 24	
	W	P	W	P	W	P	W	P
Hexane			0.9785	0.9433				
2-Butanone								
3-Methylhexane	0.9715	0.6010	0.9275	0.0475	0.8407	0.0189	0.9183	0.1515
Benzene	0.9628	0.3853	0.9861	0.9586	0.9745	0.7953	0.9834	0.9666
Heptane	0.9700	0.5609	0.9716	0.6172	0.8501	0.0016	0.9673	0.5705
Toluene					0.9853	0.9971		
Octane	0.9052	0.0141	0.8716	0.0022	0.9337	0.4011	0.9196	0.1600
Ethylbenzene	0.9837	0.9739	0.9507	0.1989			0.8283	0.0146
m,p-Xylenes	0.9837	0.9739	0.9542	0.2351	0.9207	0.0380	0.9879	0.9893
Nonane	0.9837	0.9739	0.7890	0.0001				
o-Xylene	0.9441	0.2998	0.9413	0.1246	0.9281	0.2120	0.9429	0.3016
Decane			0.9604	0.7516				
Limonene			0.9727	0.6361	0.9647	0.4362	0.9751	0.7572

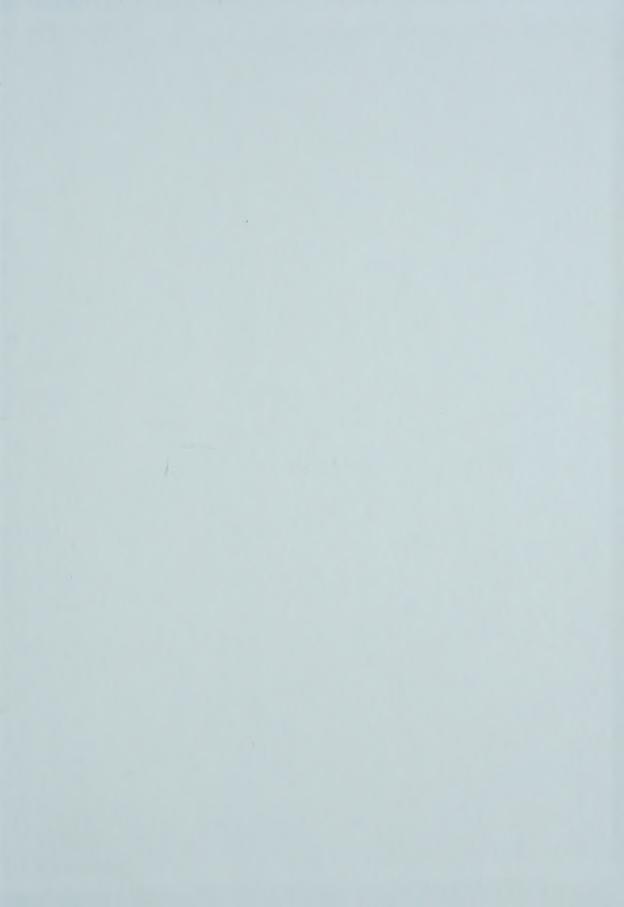














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